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DIAMONDS
WROUGHT
BY
MAN



MIR PUBLISHERS MOSCOW



SCIENTISTS
TO
SCHOOL-
CHILDREN

Б. В. Дерягин

Д. В. Федосеев

АЛМАЗЫ

ДЕЛАЮТ

ХИМИКИ

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DIAMONDS

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Translated from the Russian by
Nicholas Weinstein



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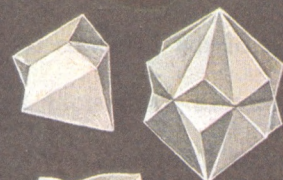
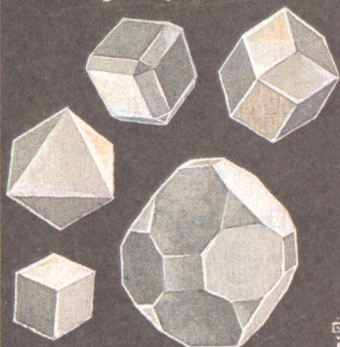
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Morphology of Diamond

Single crystals

Compound crystals

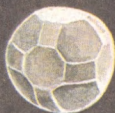
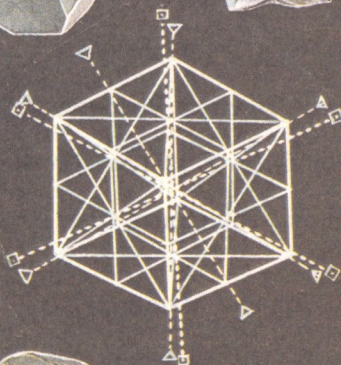


Twin crystals

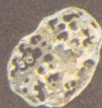


Flat-faceted

Rounded



Aggregates



Foreword

It was May of 1973. During a session of the Presidium of the USSR Academy of Sciences, members were keenly interested in a report on the synthesis of the diamond. Afterward, a ring decorated with synthetic diamonds was put on display. The diamonds had been made by chemists from Kiev.

The famous Soviet geochemist and mineralogist, Alexander Yevgenyevich Fersman, full member of the USSR Academy of Sciences and a great expert on precious and semiprecious stones, once wrote: "The diamond has been known to mankind for about five thousand years, and man has been fascinated and allured by the beauty and dazzling brilliance of this remarkable stone over these fifty centuries, constantly adding new pages to its enchanting history...." The synthetic diamonds from Kiev are one of the pages in the modern history of this astonishing mineral, a history which man has begun and continues to write in our time.

This page of diamond history was begun over two centuries ago, when the French chemist Antoine Laurent Lavoisier showed that diamond is in some way related to carbon. The end of the 18th century marked the beginning of persevering attempts to obtain this mysterious variety of crystalline carbon artificially. The history of this search abounds with the names of famous investigators. E. Lundblad, H.T. Hall, J.B. Hannay, V.N. Karazin, H. Moissan, L.F. Vereshchagin, K.D. Khrushchev and many other Russian and foreign scientists made invaluable contributions to our knowledge of the nature of the diamond, and tried to devise feasible techniques for its production.

Synthetic industrial diamonds (i.e. those applied for

various purposes in various industries) are no novelty in our time. They serve mankind faithfully, enhancing the advances of modern science and engineering.

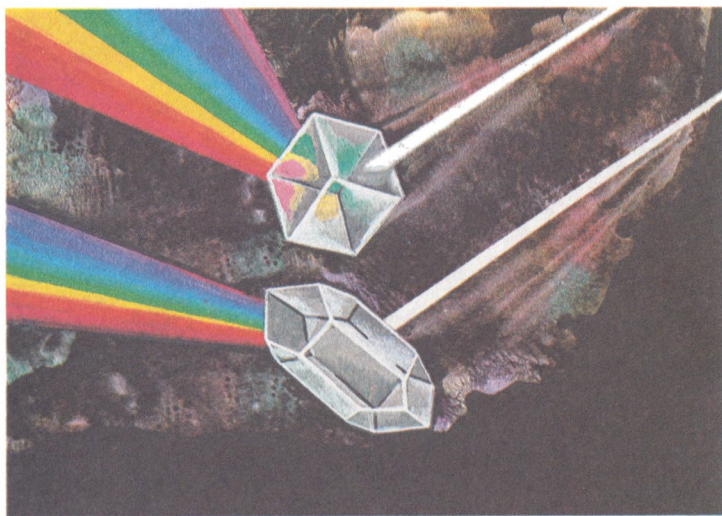
Today, scientists of many countries are working on techniques for making large gem diamonds. Undoubtedly, they shall soon find efficient methods for their production.

But before this time comes, many events will occur in the history of diamond synthesis. Investigators are faced with much time-consuming research aimed at improving existing procedures for diamond synthesis, such as the high-pressure method or the growing of diamonds and seed crystal enlargement from a carbonaceous gas. They are also engaged in the development of new techniques based on the latest advances in various branches of science.

We have made an attempt in this book to tell the story of how close cooperation between chemists and physicists enabled mankind to produce synthetic diamonds, a wonder-material that previously could only be envisioned.

King of the Minerals

Diamond as a precious stone. Diamond is rightfully regarded as one of the most expensive minerals. Even tiny diamond slivers cost hundreds of times more than their weight in platinum or gold, whereas large diamonds are practically priceless compared to other precious stones. By cutting and polishing, a rough diamond is transformed by diamond cutters into a gem diamond notable for its amazing property of converting a beam of light into a lively rainbow. At the slightest movement, such a stone sparkles and is iridescent with a play of gay colours in lovely hues.



Diamond (*above*) and quartz (*below*). The fire and sparkle of diamond are due to the strong refraction of beams of light in the crystal. After passing through diamond the rays diverge in fanlike fashion. This is called *dispersion*.

As we know from school physics, a beam of white light is made up of beams of various colours. They comprise the spectrum of which the outermost are the red and violet beams. In passing through various transparent substances, a light beam is differently refracted and, moreover, each colour has its own definite kind of refraction. The substance transmitting the beams is specified by their indices of refraction and by the difference of the indices of refraction for the red and violet beams. This difference is known as the dispersion of the given transparent substance. The fire and sparkle of a diamond crystal is due to its high indices of refraction and high dispersion. A beam of



Treasures of the USSR Diamond Fund: 1. The Orloff Diamond (189.62 carats) mounted in a sceptre in the XVIII century.

white light, after refraction in a diamond, produces a more widely divergent bunch of spectral rays and, therefore, a more prominent interplay of rainbowlike colours.

With respect to clarity (transparency) diamond is divided into several categories. In the clearest crystals no imperfections are visible even under ten-power magnification; such diamonds are said to be flawless. The least transparent crystals, with defects visible to the unaided eye, are said to be heavily flawed. But even the most perfect diamond crystal (called a diamond of the first water) has various inclusions and impurities. Their presence determines the absorption of beams from



2. The Shah Diamond (88.7 carats) from the XVII century. It is of great historical, artistic and financial value.

various parts of the spectrum by the stone. This, in its turn, also influences the colour effects of the diamond.

Generally, it is colourless diamond that brings the highest price. But diamond crystals of bright pure tones of red, green, blue or orange colours are found in nature. They are called “fancy colour” diamonds and are valued even higher than the colourless ones.

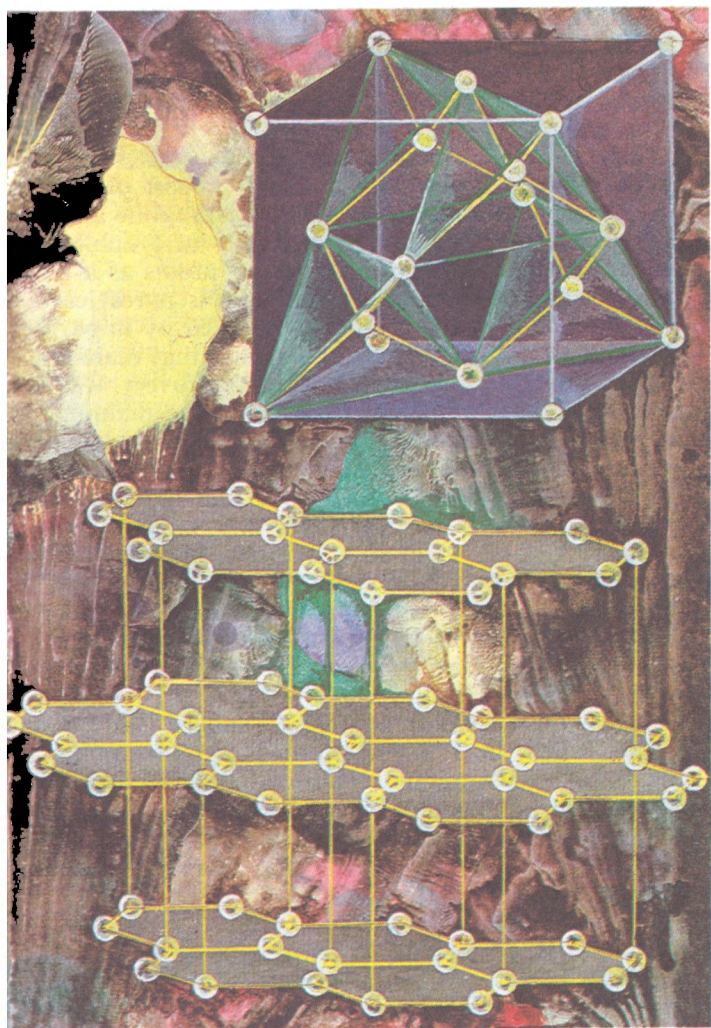
The value of a diamond crystal depends, not only on its clarity and colour, but on its cut, the quality of polishing and the shape of the finished gem. The most frequently used are the rose, marquise, brilliant and pear cuts. The brilliant cut is the most popular one because the stone acquires maximum lustre, and is full of fire and sparkle.

This is obtained by imparting to the diamond a shape having 58 facets whose relative positions are formed with high geometric precision.

The cost of diamond is also determined by its weight: the larger the stone, the higher its price. The weight of a diamond is measured in special units called carats (one carat equals 0.2 gram). Used in ancient times as a measure was the carob seed which is of more or less uniform weight. These seeds grow on carob trees (*Ceratonia siliqua*) and are called *keration* in Greek. This is the origin of the word "carat". The largest diamonds reach 200 and more carats. The most famous of these are the Hope, Orloff, Koh-i-noor, Great Mogul and the Shah.

The extraordinary beauty of the diamond has become the cause of the complicated fate of many stones. Over the centuries various magical properties have been attributed to these amazing gems. They are supposed to bring good luck and happiness; to be a symbol of faithful and eternal love; to impart courage and to inspire fear. Especially large diamonds became tokens of power and great wealth. Their chronicles are full of fabulous events, thefts and deceptions. Each large stone has its own multi-faceted history. The Koh-i-noor Diamond, now in the crown of the Queen Mother of Great Britain, belonged, in the 19th century, to Shah Shuja, an Afghan prince. To keep this matchless treasure, Shuja endured blinding and torture, but lost it after all. The fateful Hope Diamond brought misfortune to all of its private owners, including Louis XIV of France, Henry Thomas Hope, Habib Bey and the

The crystal lattice of diamond (*above*) and graphite (*below*). The astounding properties of diamond are associated with its crystal structure.



American woman Evalyn Walsh McLean. It is now on display in the Smithsonian Institution of Washington. Legends associate murders, conspiracies and disastrous mishaps with this most beautiful steel-blue stone.

Composition and structure of the diamond. These legendary crystals, like all diamonds, consist of carbon, which is very abundant in nature. Both graphite and coal consist of atoms of carbon; molecules of graphite and coal have exactly the same number of atoms as a molecule of white diamond. Such diamond is purest carbon and the colour of the crystal is imparted by impurities.

Mankind did not at first understand that diamond is one of the forms of carbon. This discovery was the result of long years of investigation of the diamond by many scientists. First, Sir Isaac Newton, in studying the refraction of light by organic substances at the end of the 17th century, boldly proposed that diamond is of organic nature. Next, in 1772, the famous French chemist Antoine Laurent Lavoisier investigated the effect of sunlight, focussed by a huge convex lens, on diamond. He found that diamond burns in air and that the products of this combustion cause the same kind of turbidity in clear lime water as does carbon dioxide.

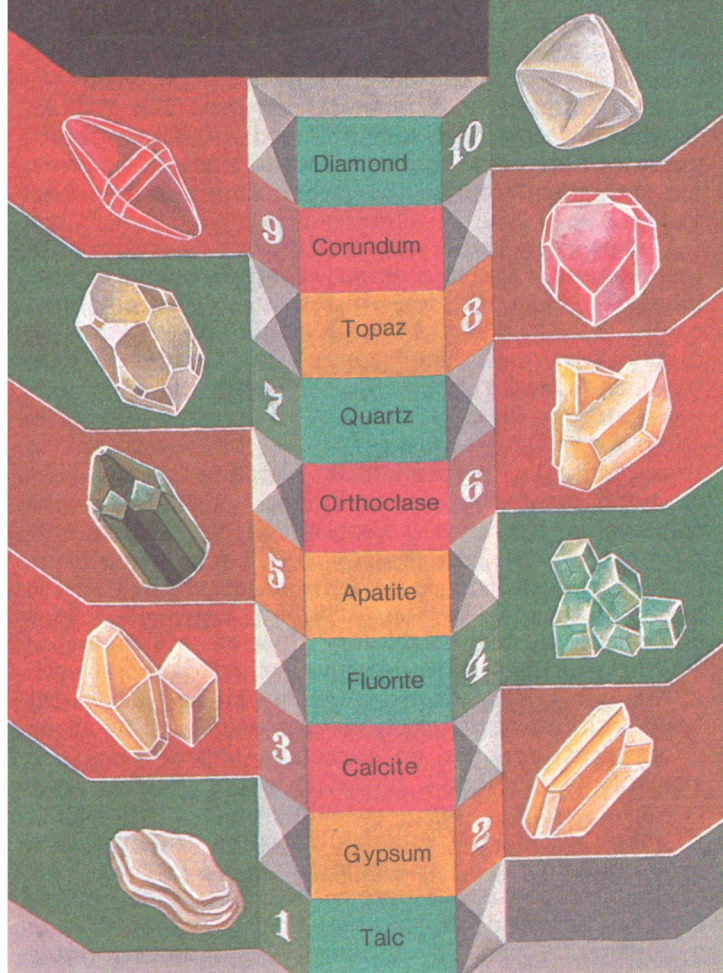
The English chemist Smithson Tennant made a step further when, in 1797, he burned equal amounts by weight of coal, graphite and diamond separately in a closed airtight golden vessel together with saltpetre. He found that in each case the same amount of "bound air" is formed. The final proof that diamond is carbon was established by the eminent English scientists Sir Humphry Davy and Michael Faraday. In 1814, with the aid of the sun and a burning lens, they burned precisely weighed diamond and graphite in pure oxygen, whose amount was just as precisely measured

in a reaction vessel. The result was convincing; they showed that only carbon dioxide is produced in the combustion of diamond and nothing else. This concise history of how the nature of diamond was established comes to its logical conclusion in 1913 when the famous Braggs, Sir William Henry and Sir William Lawrence, father and son, obtained an X-ray photograph of a diamond and revealed its internal structure, i.e. the arrangement of the carbon atoms in its crystal lattice.

It is precisely this crystal structure that is responsible for diamond's amazing optical features, and its unique physical and chemical properties. The minimal complete cell (called the unit cell) of diamond is in a cubic space lattice and consists of 18 carbon atoms, of which 8 are located at the vertices of the cube, 6 at the centres of its faces and 4 at the centres of 4 (of 8) cubes formed by dividing the unit cell by means of three mutually perpendicular bisecting planes. The diamond crystal (or space) lattice constant, i.e. the distance in the crystal after which the structure is repeated, equals 3.657 \AA ($\text{\AA} = 10^{-10} \text{ m} = 1 \text{ angstrom}$) and the closest distance between atoms is 1.54 \AA . Each atom of carbon in the diamond lattice has four equivalent closest neighbours, located at angles of $109^\circ 30'$ with respect to one another. In diamond each of the four valence electrons (per atom) has a covalent bond with one of the electrons of a neighbouring atom. A covalent bond is an especially strong one. The elements of diamond's crystal structure combine into crystals that are usually of octahedral, rhombododecahedral, icosahedral, cubic or, sometimes, a combination of these shapes.

Diamond consists of pure carbon. But carbon atoms can be arranged in another crystal lattice having a different type of atomic bond and forming

MOHS'S HARDNESS SCALE FOR MINERALS



a substance with properties drastically differing from diamond. This substance is graphite. It has a complex lamellar (layered) structure with the distance 3.39 Å between the layers. The atoms in the layers form regular hexagons having sides 1.42 Å long. The layers are oriented so that three vertices of three adjacent hexagons coincide at a point that is directly under (and above) the centre of hexagon in the adjacent layer. Therefore, complete repetition of the structure of graphite occurs at a distance twice that of the distance between the layers. Owing to its lamellar structure graphite is readily split into flakes, but the atoms in each layer are bonded together even more strongly than those in diamond.

Diamond acquired its unique properties as a result of the unusual conditions under which it was formed millions of years ago. Intense heat and huge pressures in the depths of the earth forced the carbon atoms to align themselves in a regular cubic lattice that imparted unsurpassed hardness to this mineral.

Diamond as a hardness standard. Diamond is valuable, not only for its extraordinary optical properties, which are found, to some extent, in other minerals, for example, zircon. The diamond crystal attracts the attention of scientists and engineers because of its high mechanical durability.

The mechanical durability of a crystal is determined by its hardness, i.e. its resistance to indentation or to scratching by another substance. Hardness can be measured in various ways. Each method has its hardness scale and its distribution of crystals along this scale. In any such scale, diamond is the standard of hardness.

In 1811, Friedrich Mohs, a German mineralogist, proposed his hardness scale. The Mohs scale is one of

the most widely known. It is based on the fact that a harder material scratches a softer one. Mohs selected ten minerals as the degrees, or steps, in his scale. These minerals were given numbers and arranged so that each member in the series can scratch any of the preceding members. The softest, talc, was designated (1). Then come gypsum (2), calcite (3), fluorite (4), apatite (5), orthoclase (6), quartz (7), topaz (8), corundum (9) and, the very hardest, diamond (10). Any other mineral (or, in general, any hard body, such as glass, metals, etc.) can be placed in the scale between two minerals, of which one scratches the given body and the other, on the contrary, is scratched by it. But this method is not very convenient. Much depends upon the shapes of the bodies and minerals, and how the scratches are made. Moreover, the hardness of various faces and edges of one and the same crystal can differ. In diamond, for instance, the hardest is the face of an octahedron and the least hard is the face of a cube.

Another method for measuring hardness, also involving the diamond, is widely employed. It consists in forcing a square-based diamond pyramid at constant pressure into a ground, or even polished, surface of the body being investigated. The less the area of the indentation formed by the pyramid, the higher the hardness of the specimen being tested. To obtain the quantitative hardness value (called, in this case, the diamond pyramid hardness number) we divide the force (in kg) with which the diamond pyramid is forced into the surface by the area (in mm^2) of the indentation.

The hardness number (in kg/mm^2) varies somewhat, depending upon the force applied to the pyramid. Especially large variations are obtained for bodies whose properties are not the same along the depth to which the diamond pyramid penetrates. Glass, for example, hardened by rapidly chilling the melt, has

a denser surface layer; this layer is cooled first, it contracts and solidifies. The inner part of the glass, enclosed in the “crust” that is formed, retains a state of less density. In these cases, it proves more expedient to measure the hardness with a very small indentation of the diamond pyramid. The area of the resulting indentation is then measured with a microscope having high magnification. Special instruments were developed for measuring this microhardness by M. M. Khrushchev and E. S. Berkovich of the Machine Science Institute of the USSR Academy of Sciences.

This new hardness testing technique yielded interesting data. The following hardness indices were obtained: 1100 g/mm² for quartz, 1400 g/mm² for topaz, 2100 g/mm² for corundum and 10 000 kg/mm² for diamond. It has been said that diamond is to steel as steel is to butter.

It is obvious that here also diamond is a standard of hardness. The new scale, in particular, enables us to readily specify the hardness of bodies when it is between those of diamond and corundum.

Diamond is brittle. The hardness of a substance is a measure of its durability and resistance to wear. But, though diamond has high mechanical durability, it is regarded as a brittle material. It can be easily destroyed by impacts and, therefore, has low strength.

These two important properties of the King of the Minerals—hardness and strength—have confused people down through the ages. Nor did the great poet and philosopher of Ancient Rome, Titus Lucretius Carus, escape this confusion. In his famous poem, *On the Nature of Things*, he wrote:

“And finally, those things which seem to us
Compact and hard must be composed of shapes
More hooked, and as it were with branching arms
Held deeply anchored each to each. Whereof
In foremost rank doth stand the diamond stone
That’s adamant against all shatt’ring blows,
And stubborn flint, and iron’s hardy strength,
And brass that on our doors doth shriek aloud
Its protest.”*

But Lucretius was in error; diamond fears blows! It is specifically this property—brittleness—that hinders the use of diamond crystals in cutting tools for machining surfaces that are interrupted by holes and grooves. Such a tool is subject to impacts when it cuts across a hole and hits the other side.

Diamond is chemically stable. It has extremely high chemical stability. Diamond is not dissolved in even boiling sulphuric, nitric or hydrofluoric acid, or in their mixtures, which have a destructive effect on other minerals. It cannot be damaged by boiling perchloric acid, which readily dissolves graphite. Diamond is slowly oxidized in an alkaline melt, and is more stable than graphite when it is oxidized by oxygen. Neither molecules nor atoms of hydrogen have any effect on diamond, whereas graphite readily turns into a gas in interaction with hydrogen atoms.

When shielded from oxygen, diamond can withstand short-term heating even up to 2000°C. But in a medium in which oxygen is present, diamond is readily oxidized at temperatures above 1500°C, and is converted into graphite.

* Slightly revised from the translation by Charles E. Bennett. (Tr.)

This property of diamond limits the cutting speeds in machining materials with diamond-tipped tools. At high cutting speeds, the diamond tip of the cutting tool is heated by friction and is oxidized by the oxygen in the air, leading to chemical wear of the diamond tip.

While the mechanical hardness and chemical stability of diamond crystals were previously valued only in making jewelry, with the beginning of industrial applications of diamond, these features have played a special role. Since, as mentioned before, diamond is the hardest substance found in nature, it can be used, not only for determining the hardness of other substances, but as a cutting material for machining other materials by turning, drilling, boring, coarse and fine grinding, polishing, etc.

Of especial importance in applying diamond in certain new techniques are other unique properties such as its unsurpassed heat conduction in combination with high electrical resistance. At temperatures above 100 K (degrees on the Kelvin scale), diamond has a thermal conductivity even higher than those of silver and copper, in conjunction with an extremely low thermal expansion. These features enable diamond to withstand rapid heating by external heat sources.

Diamond is an excellent insulating material and is therefore in high demand in microelectronics. It suffices to impart semiconductor properties to certain parts of the surface of a diamond, and it can be used in a microcircuit. Diamond crystals also find other applications in the field of radio electronics.

Thus diamond, continuing its century-old history as the most beautiful precious stone, acquires various new specialties.

What are diamond's professions and trades?

Diamond's Professions and Trades

Diamond, the workman. Natural diamonds may be of various quality. Those suitable for jewelry are usually cut to make gems. Lower quality natural diamonds are considered to be industrial stones and are extensively used in the whole field of engineering practice. Approximately two-thirds of the diamonds retrieved by mining are industrial stones.

Diamond has been used since ancient times for working hard materials. Diamond-tipped tools, in particular, knives with diamond cutting edges, were widely used in ancient India. In China such tools were used for carving jade. Some historians contend that Egyptians used diamond tools six thousand years ago in building the pyramids. From time immemorial mankind has made use of diamond for grinding, polishing, drilling, boring and cutting various hard materials that simply could not be worked by other means.

There are almost no products of up-to-date industry that never came in contact in some way with diamond during their manufacture. This is especially true for operations in which an exceptionally high quality of machining is required, for instance, the precision machining of small watch parts. Workpieces machined by a single-point diamond turning or boring tool frequently require no subsequent finishing operations. Natural diamonds are also extensively applied for tools that operate under extremely severe conditions, for example, drill bits for oil-well drilling. Diamond drill bits are capable of excellent performance in cases when other boring tools quickly dull and must be replaced. They are being successfully employed, for instance, in drilling the early crystalline rock of extra-deep bore

holes in the Kola Peninsula. The hardness of diamond is made use of in the machine tool industry, in stonecutting, in ceramics manufacture, and in plants for making prefabricated reinforced concrete components and glass. It is practically impossible to list all the industrial trades of diamond.

Diamond belongs to the class of abrasive materials (from the Latin word *abradere*, meaning: *ab-*, away + *+radere*, to scrape). Abrasives are made of substances that have high hardness, strength and wear resistance, and whose particles are suitable for machining workpieces by cutting microscopic chips (grinding) and by finishing with some abrading process (honing, lapping, polishing, buffing, etc.). Besides diamond, other abrasives include cubic boron nitride, corundum, emery, silicon carbide and others. Abrasive materials can be crushed into powder or dust of various grain size and used in the free or bound state as abrasive tools.

Abrasive tools are ones in which a very great number of grains (for instance, of diamond) are held by a suitable bond. Each grain is a cutting element; the tool has a huge number of these grains, thereby ensuring high efficiency. When some grain is dulled and is broken out of the bond, the remaining grains continue to operate. The bond is always much softer than the abrasive grains, and without them the bond would be immediately worn away. But the host of hard grains protect the bond against abrasion by the surface being machined. A vital condition for high working capacity of diamond abrasive tools is a tight, firm junction between the bond and diamond grain. If this junction is weak, the grain simply falls out, or is easily torn out, practically without having done any useful work. To avoid this, various intermediate layers are applied to the surface of the diamond grains. Their

purpose is to join the grain more reliably to the bond by increasing the cohesion between them.

In accordance with their purpose, various kinds of bonds are used for diamond tools. A rubber bond, based on synthetic rubber with various admixtures, is used in making thin flexible grinding wheels for finishing operations. A vitrified bond (made of refractory clay, feldspar, quartz and other components) is used in all cases when its increased brittleness is no obstacle and operation is smooth without possible impacts. A resinoid bond, consisting chiefly of formaldehyde resin, is applied for tools operating at comparatively low temperatures. Abrasive tools with a metal bond are required for operation under the most arduous conditions.

Soviet industry produces about two thousand types and sizes of diamond tools, effectually meeting all requirements of engineering. For example, diamond grinding wheels are designed for grinding and sharpening carbide-tipped and hardened steel single-point tools, as well as for directly grinding workpieces in grinders and automatic transfer machines. Diamond grinding wheels may be of various shapes: straight wheels with a straight face, recessed straight wheels, tapered wheels, beveled-face wheels, wheels with a semicircular convex face and many others. Also available are cylindrical mounted wheels for internal grinding, diamond needle files and honing sticks, diamond cut-off wheels, diamond-coated abrasive belts, and diamond tools for truing and dressing grinding wheels. Diamonds find use both in the industrial plant and in the household. The local haberdasher's shop even sells diamond nail files.

The diamond concentration in various tools may vary. A diamond flaring cup wheel, for instance, used for sharpening cemented-carbide single-point cutting

tools, can have a diamond concentration of 50, 100, or 150 percent. You should not be confused by a concentration exceeding 100 percent. A diamond content of 4.4 carats per cubic centimetre, or 0.88 g/cm^3 , of the diamond-carrying layer (consisting of diamond grains, bond and a filler of solid minerals) is conventionally taken as a concentration of 100 percent. This concentration corresponds to 27 carats per cubic inch, first adopted in the USA. It can be readily shown that at a 100 percent concentration, the diamond grains occupy 25 percent of the total volume of the layer. The density of diamond is 3.52 g/cm^3 . If we divide 0.88 g/cm^3 by the diamond density we obtain 0.25. This figure is independent of the kind of bond employed.

Diamond tools enable the cutting speed to be increased and the surface quality to be improved in machining all possible materials. These include some that are of prime importance in up-to-date engineering and are extremely difficult to machine without making use of these marvelous crystals. Hence, the level of diamond application is an indication of the volume and efficiency of a country's industrial power. Of interest in this connection are the calculations of V. N. Bakul, late Director of the Kiev Institute of Superhard Materials, given in his booklet "Diamond: Its Past and Present". He defined the need for diamonds of a country on the basis of the amount consumed per million metric tons of steel output. According to calculations, if diamond is used in all known machining techniques with 100 percent efficiency, 400 thousand carats are required per million metric tons of steel produced. In 1970 the world steel output (not including the USSR) was 450 million metric tons, so that 180 million carats of diamond would have been required to gain all the possible advantages of diamond machining. Actually, only 45 million carats were used, i. e. only 25 percent of the vast

potentialities of diamond cutting materials had been utilized.

Incidentally, what do 450 million metric tons of steel and 45 million carats of diamonds amount to? Imagine a steel cube with sides about 400 m long and a diamond cube with sides less than 1.5 m long. Their volumes differ by a factor of over 20 million. The automotive industry manufactures heavy dump trucks, each of which is capable of moving the total annual world diamond output in a single trip.

The importance of diamond in industry is also affirmed by the conclusions of a group of American economists who contend that the industrial and military power of the USA would be reduced by one half if no diamonds were used. Thus, as we see, diamond is also a strategic material.

Diamond, the researcher. The remarkable properties of diamond enable it to find employment, not only as a workman, but as a researcher as well. Diamond is an indispensable participant in the operation of all high-precision instruments. The jewels (bearings) of all high-class chronometers are made of diamond. Certain diamond crystals are very sensitive to radiation; this property is utilized in diamond dosimeters.

Diamond is excellently perceptive to heat and cold. Diamond thermometers can instantly detect changes in temperature of thousandths of a degree. The thermal conductivity of diamond has found application in space investigations. Scientists of the USA National Aeronautics and Space Administration (NASA) have used diamond to determine the temperature of stars. A jet plane, flying in the upper layers of the atmosphere, carries a telescope that is focussed on a definite star. A diamond disk, as thin as paper, is placed in the path of the rays. It senses the changes in

heat, imperceptible by any other means, and transmits signals to a special detector, which enables the temperature of the body in distant space to be measured.

But the service rendered by diamond to space research is not confined to the above examples. Diamond is the only material that is transparent to infrared rays and can withstand both the intense cold and vacuum of space, as well as unbearable heat and pressure, hundreds of times greater than those encountered under ordinary conditions on earth. American scientists furnished a probe for investigating the aggressive atmosphere of Venus (with its 500°C temperature and 100 kgf/cm^2 atmospheric pressure) with a diamond window. Infrared radiation passed through this transparent window, mounted in a metal frame, to instruments that could analyze the atmosphere of this planet and, in particular, to determine more accurately the composition of the thick Venusian clouds.

Diamond, the researcher, is much younger than diamond, the workman. But, without any doubt, we foresee its brilliant future. It is based on the fact that in increasing our knowledge of the world, in our investigations of the earth and space, we more and more often encounter as yet unexplained phenomena. They can be cleared up only with the aid of more and more complex, and, especially, more precise and sensitive instruments. It will hardly be possible to manage here without the assistance of the King of Minerals, which is already indispensable in many production and research techniques.

Unfortunately, however, diamond is an extremely rare mineral and diamond mining is a very expensive operation. Hence attempts to produce diamond by some synthetic procedure were begun many years ago.

But, before synthesizing this supermineral, it was necessary to lay a long and wearisome siege to its natural secrets, a siege which, very likely, has not yet been raised. We try to understand in finest detail the natural mechanism by means of which diamond is formed; then we make every effort to exactly reproduce the processes motivating this mechanism, first in the laboratory and, finally, in an industrial plant.

What have we already found out about natural diamond?

Natural Diamonds

Primary deposits. These are the main kind of diamond deposits. As a rule they are diatremes, which are tubular cavities in the earth's crust filled with deep-seated rock called kimberlite. Diatremes, usually called pipes, are almost vertical and intersect other kinds of rock deposits, some being old crystalline rock and some—sedimentary rock—being deposited more recently (limestones, coal, clay rock, etc.). Such diamond pipes are located, for example, in South Africa and in the Yakutsk Republic in the USSR. The pipes are of circular or elliptic cross section with diameters from tens to hundreds of metres. The kimberlite in the pipe contains the diamonds. The diamond content rarely exceeds thousandths of one percent of the total mass of the rock. Diamonds are nonuniformly located in the kimberlite. Most often found are single crystals, less frequently found are aggregates. Never do we find a large accumulation of diamonds at one place.

Today, practically everything is known about the origin of diamond pipes, but the formation of the diamond itself remains a riddle. Most scientists contend that the kimberlite pipes were formed by an upheaval

of magma rich in gases. Most likely the magma rose along crevices in the rock and, when the pressure of the layer of the earth's crust remaining up to the surface became less than the pressure in the magma, an explosion occurred.

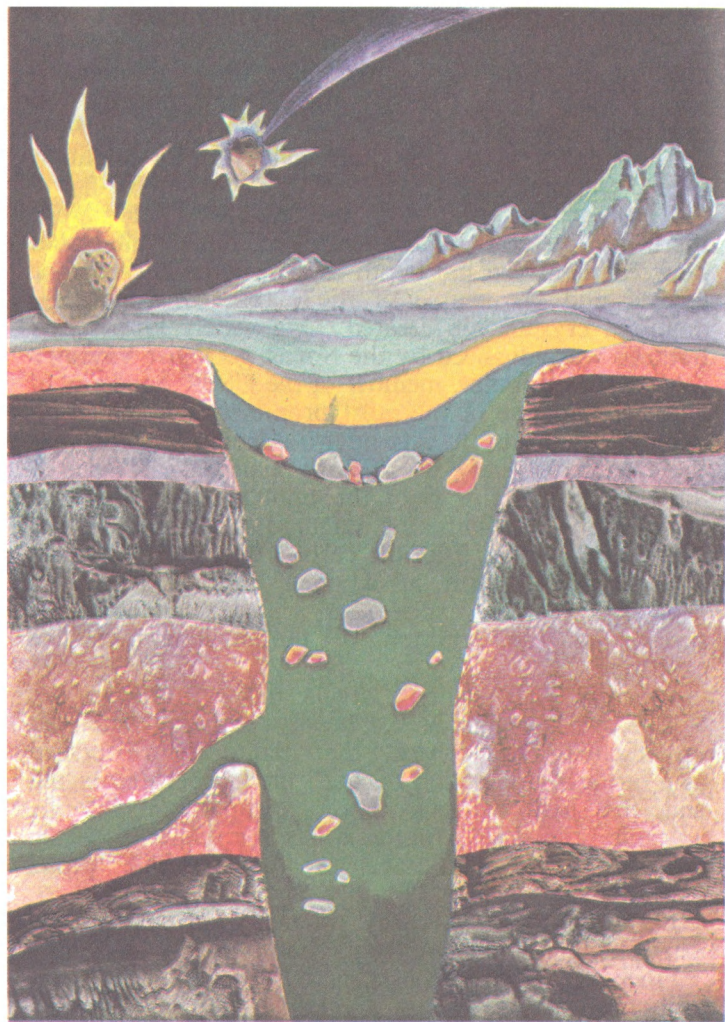
This theory gives the diatreme its more common name: volcanic pipe.

No theory exists as yet for the origin of diamond, but there are several hypotheses. The main differences between them are the depth at which the diamond is formed and the source of the carbon of which the diamond crystals are created. One widely known hypothesis was advanced by the Soviet geologist Vladimir Stepanovich Sobolev, member of the USSR Academy of Sciences and one of the most prominent specialists on diamond deposits. It was he who first suggested that there could possibly be primary diamond deposits in Siberia. Dr. Sobolev is of the opinion that diamonds crystallize in the kimberlite magma itself, in early stages of its development, from the carbon dioxide it contains. The diamonds form at a great depth, before the explosion mentioned above, and are then carried to the surface by the eruption of the magma and the explosion.

Recently, a hypothesis advanced by V.G. Vasilyev, V.V. Kovalsky and N.V. Chersky is being intensely investigated. They contend that diamonds are formed as a result of interaction between the kimberlite magma and the hydrocarbons that accompany it in the volcanic pipe. This hypothesis has the diamonds being formed in a later stage of the volcanic pipe's development.

Besides these two, many other hypotheses on the origin of diamonds are being discussed by scientists.

Diamond pipes were first discovered in South Africa in 1871 near the town of Kimberley, and were named



kimberlite pipes. Before the discovery of the Yakutsk deposits, the pipes at Kimberley were practically the only examples of primary deposits. On August 21, 1954, a Soviet woman geologist, L. A. Popugaeva, discovered "Zarnitsa" (Summer Lightning), the first diamond pipe in the USSR. A year later, Yu. I. Khabardin and B. N. Yelagin explored the "Mir" (Peace) diamond pipe. This was followed by the discovery of many other workable deposits in the Yakutsk Republic. A group of geologists were awarded a Lenin Prize for these discoveries in 1957.

Primary diamond deposits of the kimberlite type are of commercial value. There also exist primary deposits of small diamonds; they are of the peridotite type and are confined to deep-seated rock. These deposits cannot be worked profitably at the present time by commercial methods.

Placer deposits. By far the greatest amount of diamonds (over 80 percent of the world output) are mined in placer deposits. Placers are of various origin and are associated with the weathering of primary diamond-bearing rock and the displacement of the diamonds over huge distances by wind, water and glaciers. This may lead to natural enrichment. Cases have been recorded in which up to a thousand carats of diamonds were retrieved from a single cubic metre of soil. The number of high-grade and large diamonds are always greater in placers than in primary deposits. This is due to the separation of the large crystals from the fines and chips during transport.

A primary deposit of diamonds, called a kimberlite pipe. Shown above is a meteorite that fell to the earth. Diamonds have been found in meteorites.

About 36 million carats of diamonds were mined in 1970 in the capitalist and developing countries. This included about 14 million from Zaire, 1.5 million from the People's Republic of the Congo, about 2.5 million from Angola and over 8 million from the Republic of South Africa and Namibia (South-West Africa). Capitalist production is associated with a predatory attitude toward the natural resources of the underdeveloped countries in general, and toward valuable mineral deposits of colonial and developing countries in particular. V. Korovikov, correspondent of the Pravda newspaper, wrote in 1977 about the ravaging of Namibian mineral wealth by international monopolies. He said: "The most profitable business in Namibia is the mining of diamonds in coastal sands and old marine terraces. This is being done with powerful, up-to-date mining equipment by the Consolidated Diamond Mines, a branch of De Beers, a world diamond monopoly owned mainly by its board chairman Harry Oppenheimer. This corporation retrieves about 1.5 million carats of valuable crystals annually from Namibian soil. Namibian diamonds are famous in that the greater part are gem stones. Very significant data can be found in the last report (for 1976) made to the stockholders of De Beers. Namibia produced 10 percent of the total diamond output of the concern, providing 25 percent of its fantastic profits. In 1976, after paying taxes, these profits amounted to 337 million rand (almost 400 million American dollars). These fabulously rich placers of Namibia are being most intensively worked. As a result, a considerable part of the placers have already been depleted, and the whole diamond-bearing region to the north of the mouth of the Orange River will be despoiled in the next ten to fifteen years."

Lean diamond placers, having no commercial value,



Diamonds from placer deposits.

can be found in many countries. Single small diamond crystals can be found practically all over the earth. In the USSR they are found, not only in Siberia or the Urals, but on the Central Russian Uplands and in the Ukraine as well. Such finds are sometimes connected with the fall of gigantic meteorites to the earth in prehistoric times.

The presence of diamonds in meteorites was first established in 1888 by two Russian scientists, lecturers of the St. Petersburg Forestry Institute, M.V. Yerofeev and P.A. Lachinov. They discovered diamonds in a stony meteorite that had fallen near the village of Novy Urei (now called Karamzinka in the Gorky Region). Such meteorites are now called ureilites.

In 1891 American scientists found diamonds in

fragments of the meteorite that fell in Arizona and formed the Meteor Crater. This enormous celestial body left a circular depression about 1200 m wide and up to 184 m deep. According to the estimates of specialists, the initial mass of the meteorite could be from 50 thousand to 3 million metric tons, and its velocity at impact was anywhere from 12 to 20 km/s. The Arizona meteorite belongs to the iron, or siderite, type, and investigators collected many tons of meteoric iron at the site where it fell. This iron was preserved primarily because of the superstitions of the local Indians who held the crater and everything related to it to be sacred. The inhabitants of Europe usually used any meteoric iron they found in ancient times, and the first iron applied by man for household purposes was of meteoric origin.

The diamonds in meteorites are small microcrystals, several micrometres in size. Of most interest is the fact that along with diamond having the usual cubic structure, crystals of a new, hexagonal modification are also found in meteorites. These crystals were named lonsdaleite, after Dame Kathleen Lonsdale, an English crystallographer and well-known investigator of diamond structure.

About one-third of the total amount of diamonds found in the Arizona meteorite were of lonsdaleite.

Meteorite diamonds were formed as a result of collisions of these bodies, travelling at immense velocities in space, with one another (chiefly in the asteroid belt), or with the earth. The high temperatures and pressures reached in such collisions set up conditions for crystallizing diamond from the carbon in the meteorites.

When meteorites fall to earth they leave gigantic hollows, known as meteorite craters. In them one can find cloudy diamond grains of irregular shape that

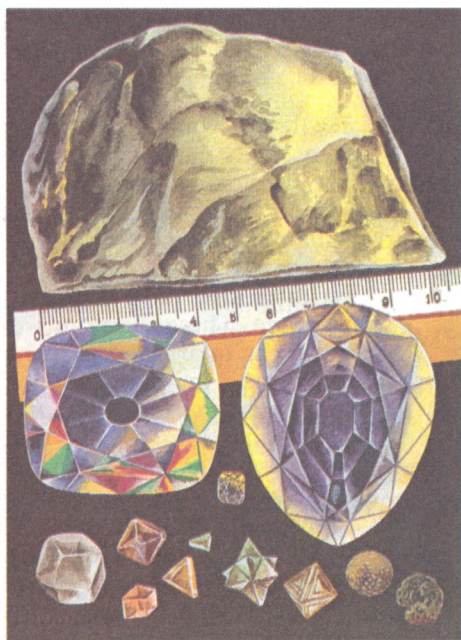
resemble fragments. Such diamonds are obviously formed in the fall of an enormous meteorite on carbonaceous rock.

Diamond classification. Under diverse conditions diamonds of different kinds can be formed, and each variety can have its field of application. For precise identification and proper practical investigation of one or another kind of diamonds, a classification, based on a scientific approach, is a vital requisite.

Mankind was first interested only in large diamonds of which gems were made. These diamonds are known world-wide, they are works of art, and each has its own name. But in our time, in connection with the applications of diamonds in industry and science, a sharply defined classification of all the types is necessary, and it is no simple matter to devise such a classification. Much work in this line was carried out by Yu.L. Orlov, a well-known Soviet scientist. He divided all natural diamonds into two large groups: single crystals and polycrystals (polycrystalline formations), and the groups into ten varieties.

The first five varieties of single-crystal diamonds include both well-faceted colourless stones and coloured stones with various impurities and low transparency.

The polycrystalline kinds of diamond include ballas diamonds, bort and the carbonado. Ballas diamonds have a radiate-fibrous structure and are almost spherical in shape. Bort also consists of aggregates of separate diamond crystals. Carbonado, also called black diamond and carbon diamond, is a fine-grained diamond aggregate. It occupies a special place in the classification, being the tenth variety. Carbonado greatly differs from other kinds of diamond, and can be regarded, not only as a variety of polycrystalline



The Cullinan Crystal (3106 carats), the largest diamond ever found in nature. In the middle are two of the 105 gem stones cut from the Cullinan: Cullinan I (530.2 carats) and Cullinan II (317.4 carats). A one carat diamond is shown between them for the purpose of comparison. Shown below are certain natural shapes of diamonds.

diamond formations, but as a variety of diamond itself as a mineral. Carbonado consists of very fine microcrystals of diamond (of a size up to 20 micrometres) seemingly sintered together.

The classification of natural diamonds proposed by Yu.L. Orlov is a mineralogical one. An industrial or

commercial classification goes into much greater detail and consists of a great number of groups and types.

Natural diamonds, even those of the "first water" are not entirely pure and, in addition to carbon, contain various inclusions. The amount of inclusions varies, of course, in diamonds of different varieties from different deposits. The principal impurities are hydrogen, boron, nitrogen, oxygen, sodium, aluminium and silicon. Practically all the elements of Mendeleev's periodic table can be found in natural diamond.

The present book was written to describe the production of synthetic diamond, putting aside all aspects concerning the prospecting and discovery of diamond deposits, the retrieval of diamonds and their subsequent treatment. We refer readers interested in these matters to special books on these subjects. Here we only wish to call attention to a remarkable fact: many discoveries of natural diamonds were made by children. The first diamond was found in South Africa in 1867 by children that were playing with this sparkling stone. But, of course, a grownup ostrich hunter happened to walk by and took the diamond from the children. The first small diamond crystal in the Urals was found by fourteen-year-old Pavel Popov in 1829 at the Krestovozdvizhensky gold field. The first Ural diamonds were given as a gift to Baron Friedrich Heinrich Alexander von Humboldt, the famous German naturalist and geographer, travelling at that time in Russia.

People have gradually unraveled the mysteries of diamond, discovered its properties, composition and occurrence. Guesses have been made as to the conditions required for the development of this amazing crystal. When an appreciable amount of knowledge concerning natural diamond had accu-

mulated, it became feasible to realize a long-standing ambition: to produce man-made diamond. What, then, is the history of synthetic diamond?

Three Periods in the History of Diamond Synthesis

Intuitive (empirical) period. Practically as soon as it became obvious that graphite and diamond consist only of carbon, attempts to synthesize diamond began.

A well-known public figure in Russia and the Ukraine, Vasili Nazarovitch Karazin, performed experiments in which he burned coal to produce diamond. Unfortunately, details of his research have not been preserved. It is known, however, that these were the first serious experiments in this line and that in 1823 he obtained small crystals that were extremely hard. Laboratory tests indicated that they were identical to diamond.

In 1880 experiments were conducted on diamond synthesis by the English scientist James Bannantyne Hannay. He filled steel pipes, of the size of cannon barrels, with a mixture of hydrocarbons with the salts of lithium and sodium, and sealed off the pipes by means of welded covers at their ends. The pipes were heated and kept red-hot for a whole day, and only a small amount of them withstood such severe treatment. In one of the pipes that did not burst, Hannay found a dozen shiny crystals, which could scratch corundum (the next hardest mineral in the scale, in which it follows diamond). These crystals had a density of 3.5 g/cm^3 , burned without residue in the flame of a burner, and did not dissolve in hydrofluoric acid.

The experiments of the French chemist Ferdinand Frédéric Henri Moissan brought him world fame.

Widely used in his research was the electric furnace that he had invented. Prof. Moissan dissolved pure carbon—charcoal from sugar—in boiling iron, and then poured this mixture into cold water. Moissan's reckoning was as follows: iron in the heated state dissolves considerably more carbon than in the cold state. Hence, in cooling, excess carbon precipitates in the free state in the form of graphite or maybe in the form of diamond. Iron, moreover, in contrast to the majority of metals, does not shrink in solidifying; instead it expands in volume. The outer crust that solidifies immediately upon cooling prevents the inner layers from expanding, compresses them and thereby leads to a substantial increase in internal pressure. But a high pressure is exactly what is required to convert the graphite into diamond, because graphite is less densely composed of atoms than diamond. This, according to Moissan, provides favourable conditions for the crystallization of diamond.

The ingot of cast iron that was obtained (the dissolving of carbon in iron leads to the formation of cast iron) was dissolved for a long time in various acids. As a result, Moissan separated out several grains, mostly black. These grains scratched corundum, burned almost completely in oxygen and had a density over 3 g/cm^3 . Prof. Moissan reported on his experiments in 1899.

In this same year, Prof. Konstantin Dmitrievich Khrushchev, of the St. Petersburg Military Medical Academy, read a paper on his research at a meeting of the St. Petersburg Mineralogical Society. He had also dissolved carbon in molten metal, but he had used silver. Silver, like iron, also increases in volume when it solidifies. "Subsequent dissolving of the ingot that was obtained," reported Prof. Khrushchev, "showed that a part of the precipitated carbon has properties of

diamond. Its powder consists of transparent colourless crystalline splinters and plates that strongly refract light, are entirely isotropic, scratch corundum and burn in carbon dioxide with a negligible residue of ash”.

Dozens of ideas of all possible kinds were advanced on the production of synthetic diamond. According to one proposal, diamonds should be sought in steel ingots, before they are rolled, in steel mills. Sir Charles Algernon Parsons, famous English inventor of the impulse-reaction steam turbine, dissociated acetylene, two atoms of hydrogen and two of carbon, placed in the barrel of a gun, by a bullet shot from the muzzle. Another proposal involved the electrolysis of carbon bisulphide: the sulphur was to be deposited on a tin electrode and the carbon (in the form of diamond, of course!) on a gold electrode. The world-famous English physicist William Crookes, discoverer of many phenomena in gas-discharge tubes, tried to obtain diamond in a steel bomb filled with an explosive.

We mention here only the more or less serious attempts to synthesize diamond.

In 1917, the German physical chemist Otto Ruff carefully analyzed all the published methods of diamond synthesis and came to the following conclusion: “With the exception of Moissan, nobody was successful in producing synthetic diamond. It may be that Moissan obtained synthetic diamond, but that has not been proved”.

The crystals that were taken for diamond in all of these experiments were actually carbides of complex composition and high hardness. An exception is Hannay's diamonds, twelve grains on exhibit in the British Museum. In 1943 F.A. Bannister and Kathleen Lonsdale subjected them to X-ray diffraction analysis and found that eleven of the crystals were diamond. But not all is clear with regard to the origin of these

diamonds. Hannay, himself, had said that he had added small seed crystals in some of his pipes, but that synthetic diamond crystals had been produced in pipes having no seed crystals.

A more subtle and precise investigation of Hannay's diamonds, by observing the spectrum of their luminescence when illuminated with ultraviolet light, showed that they are natural diamonds. It is possible that these diamonds were put into the pipes by Hannay's assistants to console him in his persistent attempts to achieve his aim.

Doubts about the authenticity of Hannay's results arose earlier and were based on the unsuccessful attempts to repeat his experiments and on the lack of correspondence of the conditions in his experiments with the region of stability of diamond. This region was established subsequently. But experiments carried out with the participation of the authors of the present book show that the formation of diamond can also take place in the region of its metastability.

The probability of the formation of a diamond crystal is much less than the probability that a graphite nucleus will appear, but it does exist. If in some manner the formation of graphite is prevented, crystals of diamond may appear and grow. Moreover, researchers of the High-Pressure Physics Institute of the USSR Academy of Sciences revealed the fact that the transition to diamond occurs at different temperatures and pressures for various carbonaceous materials. According to the calculations of O.I. Leipunsky, the transition from graphite to diamond requires a pressure of 50 000 atm at the temperature 1000 K, the transition from glasslike carbon at the same temperature requires only 15 000 atm.

But we have gotten somewhat ahead in our story. According to O.I. Leipunsky, "The experiments of Otto

Ruff ended the empirical period of diamond synthesis. It became clear that diamond could not be produced by guesswork. It is necessary to precisely establish the temperature and pressure at which diamond is more stable than graphite and to conduct crystallization specifically under these conditions. Determination of the conditions for obtaining diamond comprised the theoretical period in the history of the problem of the production of synthetic diamonds”.

Theoretical period. The first scientist that tried to determine theoretically the regions of stability of diamond and graphite, and to find the boundary between these regions was the German-born English physicist Sir Francis Simon. He plotted the dependence between pressure and temperature at which diamond and graphite are in equilibrium. To be more exact, Simon's results showed only the nature of this dependence, but could not be very accurate because in 1926, when he conducted his calculations, many quantities were not measured with sufficient reliability.

The Soviet researcher, O.I. Leipunsky had at his disposal very exact values of the heat capacities of diamond and graphite, as well as their combustion heats, determined in 1937 by the American physicists Frederick Rossini and Wilfrid Sidney Jessop. On the basis of their data, Leipunsky plotted the graphite-diamond equilibrium curve. This work, completed by Leipunsky in 1939, is regarded as a classical one. Its numerical results have remained practically unchanged to the present time, notwithstanding a large number of insignificant corrections and slight refinement.

Leipunsky reached one important conclusion: it is more advantageous to crystallize diamond from a solution in molten metals than by means of a direct transition from graphite to diamond. The main reason

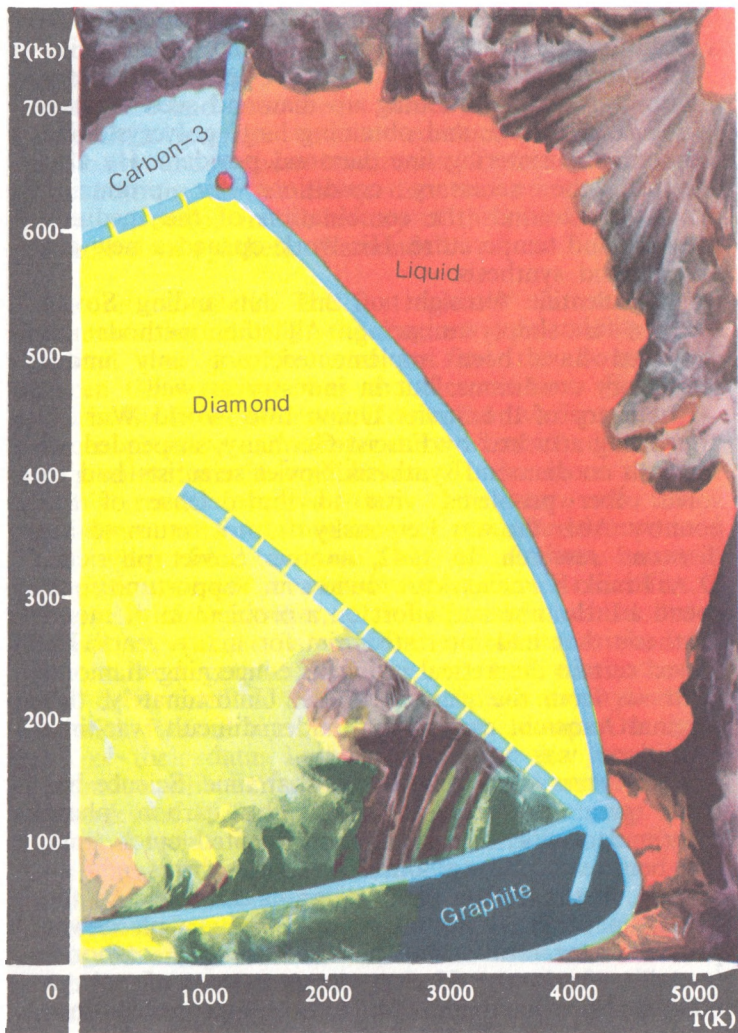
for this is the higher mobility of the carbon atoms in a solution than in the crystal lattice of graphite.

Leipunsky also mentioned other possibilities for diamond synthesis: building up diamond seed crystals in a gaseous phase, and obtaining large polycrystalline diamonds by sintering fine diamond powders. He also specified the necessary conditions for producing synthetic diamond: the combination of the medium, pressure and temperature. His work opened a new era in diamond synthesis.

The scientific foresight of this outstanding Soviet scientist is simply amazing. All the methods he proposed have been implemented, not only under laboratory conditions, but in industry as well.

The entry of the Soviet Union into World War II, after being attacked by Fascist Germany, suspended all research on diamond synthesis. Soviet scientists had to solve other problems, vital to the defense of the country. After the war Leipunsky did not return to his diamond research. In 1942, another Soviet physicist, D.A. Frank-Kamenetsky, found an opportunity to spend a little time and effort on a problem in diamond synthesis that had interested him for many years. He solved certain theoretical problems concerning diamond synthesis from the gaseous phase. Unfortunately, this original research, carried out under difficult war-time conditions, was never published.

Many years have passed since that time. Science has made great progress and now the carbon phase diagram, to which Leipunsky had devoted much time, has been extended to a million atmospheres and to 5000 K. In the carbon phase diagram calculated by the American physicist Francis Pettit Bundy, a place was provided for still another modification, carbon-3 (metallic carbon). Under a pressure of about 600 000 atm, diamond should be transformed into



metallic carbon. Experimental research of Leonid Fedorovich Vereshchagin, member of the USSR Academy of Sciences, and of other investigators, confirmed the feasibility of such a transition.

Experimental period. In 1953 a group of Swedish scientists finally succeeded in synthesizing diamond. But they did not report on their investigations, because they hoped to obtain larger crystals first. This turned out to be poor policy; they lost their priority. In 1955, the American physicists, F.P. Bundy, H. Tracy Hall, Herbert Strong and Robert Henry Wentorf, Jr., published a paper describing the synthesis of diamond in their laboratory and were acknowledged winners in the century-old "synthetic diamond race", whereas they actually placed second.

By the end of the fifties, diamond was also synthesized by Soviet scientists of the High-Pressure Physics Institute. This research was headed by L.F. Vereshchagin. M.V. Keldysh, then president of the USSR Academy of Sciences, mentioned this outstanding achievement of Soviet chemists and physicists in his report to the July Plenum (1960) of the Central Committee of the USSR Communist Party.

But the production of diamond in the laboratory is only half the battle. The main thing is to put it into regular production in industry. This is associated, primarily, with the solution of extremely difficult problems that arise in developing industrial processes for diamond synthesis. A group of scientists of the Institute for Ultrahard Materials in Kiev (now belonging to the USSR Academy of Sciences), headed

The carbon phase diagram. At a pressure of about 600 thousand atmospheres, diamond should be transformed into metallic carbon.

by V. N. Bakul, succeeded in overcoming all these difficulties. A commercial lot of diamonds and diamond components was manufactured in the experimental plant of the Institute.

Synthetic diamond is in regular production at the present time in many countries (Czechoslovakia, England, Japan, France, Ireland, etc.). Methods for synthesizing diamond are continuously being improved; engineering and industry require newer and newer kinds of ultrahard materials of higher and higher quality.

The mass production of synthetic diamond crystals proved that scientists had correctly built the theory of the diamond synthesis. What is the essence of this theory?

What Nucleation Is About

Initial stage of crystal formation. Before we take up the growth of already existing crystals, it is necessary to consider the initial stage of their formation. Assume that we have a solution of salt in water. At a given temperature water can dissolve a strictly definite amount of salt; this is said to be **equilibrium solubility**. Next we dissolve salt in water at a high temperature and cool the solution to a lower one. In this case the solution is supersaturated and salt crystals begin to precipitate from it. The ratio of the amount of substance dissolved in a liquid to the amount at equilibrium solubility is called the **supersaturation**. Supersaturation is the motive power in the crystallization process.

Now let us consider molten metal instead of water, graphite instead of salt and repeat the same operation. At low pressures (for example, atmospheric pressure)

graphite is formed, and at high pressures, diamond.

Let us conduct a similar experiment with water vapour. If we cool the water vapour only slightly in air, drops of water are formed, but if we cool it intensively, pieces of ice are formed. In all of these cases the motive power that transforms the system from one state to another is supersaturation.

These processes are studied and investigated by the branch of physical chemistry devoted to the formation of a new phase. This branch, in its turn, includes a subbranch dealing with the initial stage in the formation of a new phase: the formation of its nucleus. This subbranch of physical chemistry is called the theory of nucleus formation, i.e. the [theory of nucleation](#).

[What nucleation is.](#) The Latin word *nucleus* (nut or kernel) has had a lucky biography: it was used as the basis for a number of extremely important scientific terms. In physics nucleons are particles that form the nucleus of an atom, i.e. its central, positively charged, dense portion. In biology nucleic acid is the main component of cell nuclei. In physical chemistry nucleation is the process of forming a critical nucleus of a drop (or crystal).

We shall return somewhat later to the question of why such a nucleus is said to be critical. For the time being, let us consider what is necessary for forming a droplet from the vapour of some substance. This requires that two molecules of the vapour collide to form twins, which are joined by a third molecule, then a fourth, etc.

But such a bunch of molecules does not grow at all so quietly and continuously as, for instance, a bunch of snow from adhering snowflakes. Some new molecules may stick, while, at the same time, others may break

away. It all depends upon which process is the more rapid, adherence or breaking away of the molecules.

These processes occur everywhere around us: in the atmosphere, in liquids, in industrial apparatus, in combustion, and even in the flight of a plane leaving a trail of haze behind.

For Those Who Want More Details

Formation of a new phase. In physical chemistry, a volume of some gas, liquid or solid of homogeneous, or uniform, composition is called a phase. Usually we deal with a system of two, three or more neighbouring phases, with boundaries between them called interfaces. Hence, a glass of water has three phases: water, air and glass, and three interfaces: water-air, water-glass, and glass-air.

When the temperature of the air is lowered to what is called the dew point, the water vapour in the air becomes supersaturated and begins to condense, forming droplets. Bubbles of vapour appear inside a liquid that is heated above its boiling point. When water is cooled ice begins to crystallize. In the evaporation and concentration of an aqueous solution of some salt, crystals of the salt are precipitated. These are all examples of the formation of a new phase, and one of the special cases of such a process is the **production of diamond crystals**.

Under conditions of standard atmospheric pressure, water boils and freezes at definite temperatures. The precise values of the temperatures of these two phase transitions of water were used as a basis for constructing the Celsius (formerly Centigrade) temperature scale. One basic point of this scale is 0° , the temperature of ice formation, and the other is 100° ,

the boiling point of water. But if water is carefully cleaned to remove all dust particles and placed in the form of a suspended drop in another liquid, having almost the same specific gravity as water, with which it does not mix, the drop of water freezes at a substantially lower temperature. The record supercooling (as this phenomena is called) of water is -40°C (i.e. 40°C below zero). At the same time, water, poured into a very clean, freshly blown glass ampoule, boils at a temperature several dozens of degrees above 100°C .

An entertaining paradox is the fact that the more carefully experiments are conducted and the more thoroughly a substance is purified to remove all impurities, the larger the error obtained in constructing a thermometric scale. The reason for this paradox was revealed when the very initial stages of the nucleation of a new phase were attentively investigated.

Nucleation in vapour condensation. Vapour that is in thermodynamic equilibrium with the liquid is considered to be saturated. In a system consisting of saturated vapour and liquid, the phase interface is crossed in unit time by equal numbers of molecules from each side: the same number of molecules leave the liquid and go over to the vapour as the number that return to the liquid from the vapour. A droplet of liquid in a vapour is in equilibrium if the pressure of the surrounding vapour exceeds the pressure of saturated vapour. In other words the vapour becomes supersaturated. The amount of excess pressure depends upon the density of the vapour, the radius of the droplet, its surface tension and density. The equation of this dependence was first derived by the British mathematician and physicist, William Thompson (later Lord Kelvin).

It is evident from this equation that the smaller the radius of the droplet, the greater, for its equilibrium, the excess in the vapour pressure must be. Or vice versa: the lower the water content of the vapour, the greater the radius of the droplet must be that is in equilibrium in the vapour. At a definite value of the supersaturated vapour pressure, a droplet whose radius is less than that required tends to evaporate and, consequently, becomes even smaller. Droplets of large size, on the contrary, tend to keep growing. But a droplet of a size corresponding to the pressure of the supersaturated vapour that surrounds it is in unstable equilibrium with the vapour. Such a droplet has equal possibilities of growing further or beginning to evaporate. Such a droplet is called a critical nucleus and the process of its formation is called nucleation.

The greater the increase in energy that is required to obtain a critical nucleus, the less the probability, taking into account the random nature of the processes, for the addition of new molecules from the vapour to the molecule cluster or from the cluster back to the vapour. This increase in energy equals the difference between the surface energy of the droplet and the energy evolved in the transition of the vapour to liquid.

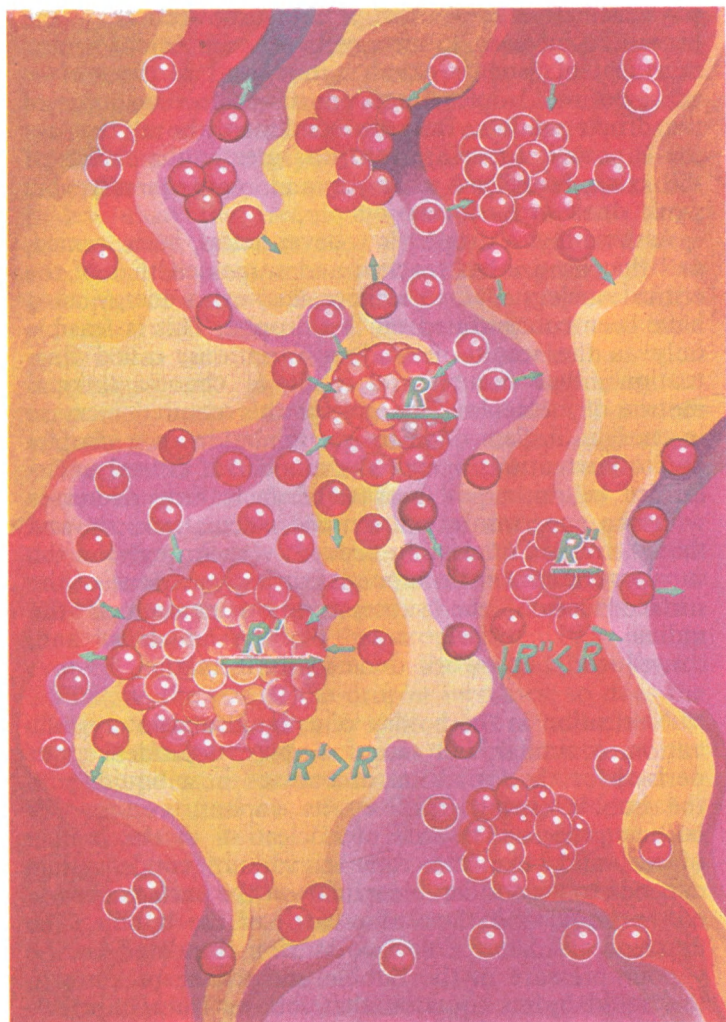
First, as the size of the droplet increases, so does the energy consumed, because the effect of the surface energy, which is proportional to the square of the droplet radius, is predominant. At a radius equal to that of the critical nucleus, the energy expended reaches its maximum value. Then it decreases because the energy of transition begins to dominate, and this energy is proportional to the volume of the droplet, i.e. to the cube of the radius. In the process of nucleation, the critical nucleus is in unstable equilibrium, like a sphere placed on a sphere.

The American mathematician and theoretical

physicist, Josiah Willard Gibbs showed that the necessary increase in energy (work done in forming a critical nucleus) is equal to one-third of the surface energy of the droplet, i.e. proportional to the square of the droplet radius. But, as mentioned above, the less the vapour is supersaturated, the greater the radius of the critical nucleus must be and, consequently, the work done in its formation.

Assume that a droplet has, nevertheless, been formed, and that its size has reached and surpassed that of the critical nucleus. But, to achieve this, extra energy must have been concentrated on this droplet. This is feasible only as the result of random variations, called fluctuations, that occur as a result of chaotic thermal motion of molecules. The greater the required increase in energy, the less often its accumulation in a droplet due to fluctuations. Hence the number of critical nuclei formed in unit time—the rate of nucleation—decreases with the supersaturation. Precise calculations showed that the rate of nucleation depends very strongly on the supersaturation of the vapour. For a given value of the surface tension, the supersaturation determines the radius and surface area of the nucleus and, consequently, the work done in its formation.

Nucleation in the boiling of a liquid and in crystallization. A similar, but more complex, dependence was derived for the formation of bubbles in a liquid, with the bubbles being filled by its vapour, i.e. for the boiling process. The rate of nucleation in the boiling of a liquid, like the rate in vapour condensation, depends to a considerable extent on the surface tension of the liquid and the surface area of the bubble. The difference is that the surface tension is related to the vapour pressure in the bubble and to the pressure in the liquid by an equation that follows from Laplace's



law. This equation expresses the difference between the pressures within the bubble and in the liquid in terms of the radius of curvature of the spherical surface of the bubble and the surface tension of the liquid.

When a crystal is formed, for example, from a solution, the rate of nucleation depends on the average surface energy of the faces of the crystal at the boundary with the solution. Here the surface area of the critical nucleus is inversely proportional to the square of the degree of supersaturation of the solution. For diamond synthesis at high pressures, molten metal is supersaturated with carbon atoms by dissolving graphite in the melt. At sufficiently high pressures (of the order of 60 kilobars) the graphite becomes less stable than diamond, and its solubility in metals (i.e. saturation concentration) exceeds the solubility of diamond. Therefore, graphite can dissolve and diamond can grow simultaneously.

Nucleation on a solid substrate. On the face of it, all that has been said would seem to contradict simplest observations: the condensation of water vapour with the formation of fog at very small degrees of supersaturation, or the boiling of water at a temperature only very slightly exceeding 100°C. But these contradictory facts can be readily explained. In the first case, the droplets of fog nucleate on particles of dust or salts which are always present in the atmosphere; in the second, the bubbles form either at suspended particles or on the walls of the vessel in which the water is being boiled. Here nucleation theory—the formation of viable nuclei of the new

Formation of the nucleus of a drop (under a microscope) from the vapour of some substance.

phase—should be modified to some extent: the presence of a substrate reduces the energy required to form the critical nucleus. This, exactly, is what is made use of in inducing artificial rain by scattering particles of salt above the clouds.

It now becomes clear why the emergence of a new phase is checked in purified substances and why the temperatures of phase transitions are shifted from their true values. Also explained, finally, is the paradox of the errors made in extremely careful conduction of experiments to graduate a thermometric scale.

Let us consider the formation of a liquid nucleus on a wettable substrate. New interfaces appear in forming the lenticular nuclei (see the figure on the following page): at the liquid-vapour boundary (with the surface area S_{12} and surface energy σ_{12}) and at the liquid-substrate boundary (with the surface area S_{13} and surface energy σ_{13}). The energy consumed in forming these interfaces is equal to

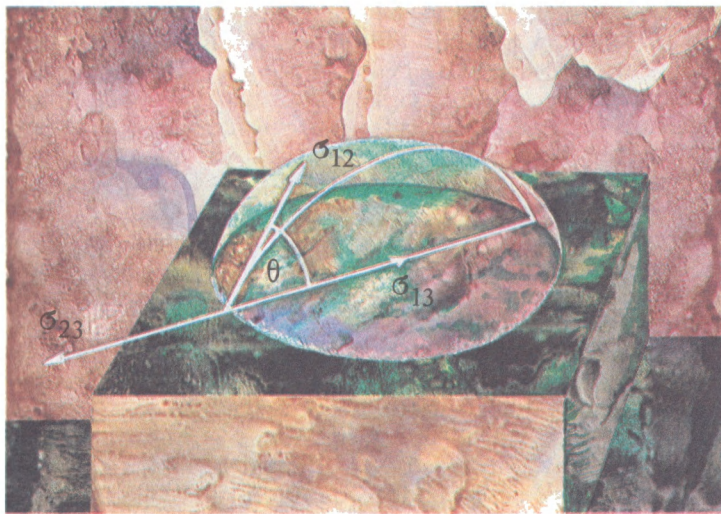
$$S_{12}\sigma_{12} + S_{13}\sigma_{13}. \quad (1)$$

At the same time, the vapour-substrate interface disappears. It has the same area S_{13} , but a different surface energy: σ_{23} . This makes the energy released equal to $S_{13}\sigma_{23}$. As a result, the energy (work) required to form a nucleus of liquid on a substrate is

$$\Delta u = S_{12}\sigma_{12} + S_{13}(\sigma_{13} - \sigma_{23}). \quad (2)$$

Assume that the contact angle, between the surface of the droplet at its edge and the substrate, is θ (see the figure). Then, from the condition of equilibrium of surface tension forces (shown by arrows):

$$\sigma_{12} \cos \theta = \sigma_{23} - \sigma_{13}. \quad (3)$$



A drop of liquid on a solid substrate.

Hence, in place of equation (2) we have

$$\Delta u = \sigma_{12}(S_{12} - S_{13} \cos \theta). \quad (4)$$

If angle θ is small and, thereby, $\cos \theta$ is close to 1, and S_{13} is only slightly smaller than S_{12} , the energy Δu becomes extremely small. It becomes clear, then, why condensation is so much easier due to the reduction of the work done in forming a liquid nucleus on a wettable substrate than condensation in the bulk of pure air. The more the surface energy is reduced in replacing contact between the vapour and the substrate by contact between the droplet and the substrate, the more easy condensation becomes.

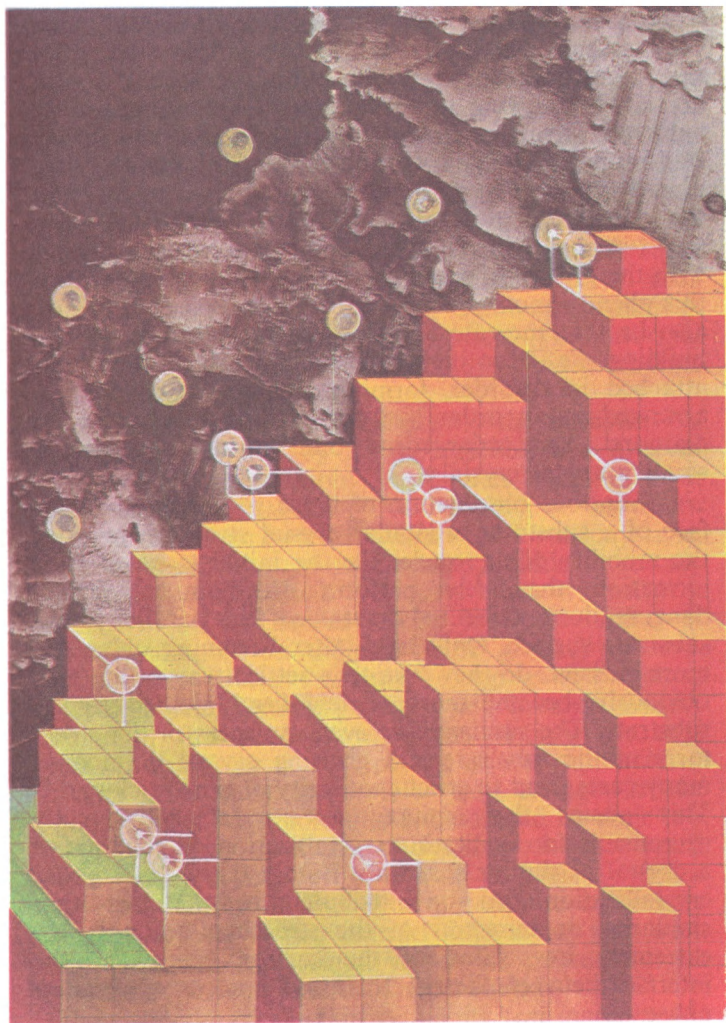
All of the aforesaid is also true for the formation of

a solid phase nucleus, i.e. a small crystal, on a substrate. The only difference is that, instead of a spherical dome, the crystal is bounded by flat faces. But very frequently, especially if formation is rapid and it is an early stage in crystal growth (and all the more so at the stage of formation of the critical nucleus), "faceting" has not had time to form, and the shape of the crystalline nucleus can be close to the shape of the droplet.

Regardless of the exact shape of the nucleus, the main conclusion we reached above remains valid: the formation of a critical nucleus is considerably facilitated if the surface energy of the substrate drops drastically when a nucleus is formed on it. Certain metals have exceptionally high surface energy. These were exactly the ones on which the formation of tiny diamond crystals was observed in the decomposition of carbonaceous gases under conditions in which small crystals of graphite would seem to be more stable.

Crystal growth mechanism and epitaxy. The maximum drop in the energy required for crystal formation and maximum reduction in surface energy (to zero) occur when the nucleus of the crystal forms on the face of a crystal of the same kind. As a matter of fact, no nucleus of a new phase is formed in this case; this is simply growth of an already existing crystal. We shall describe this process below in the discussion of diamond buildup from a gas. For the time being it is of importance to understand that buildup can also occur at low pressures, when diamond is a thermodynamically unstable form of carbon.

Epitaxy. New atoms become attached as if they continue the "brickwork" that previously existed.



To clear up the possibility of this, it would seem, paradoxical process, we shall reason as follows. Carbon atoms are deposited on the surface of the diamond crystal. But, owing to the action of the atoms of the substrate, arranged in a definite order, the new atoms build up as if they continue the "brickwork" that already exists. The capacity of crystal faces to facilitate the depositing of small crystals of almost the same structure on them is called epitaxy. If we are dealing with the growth of small crystals of the same substance, this phenomenon could be called "autoepitaxy". It may also be that the rate of arrival of new "bricks" to the building site is too high and, in the rush, they become attached in disorder, forming amorphous carbon, or arranged in an order simpler than that required for diamond. This order corresponds to the structure of small graphite crystals.

Continuous observation of the crystal nuclei on the face of a substrate of similar crystal structure revealed the mobility of the nuclei. In the initial stage of their formation, the nuclei perform Brownian movement, dancing along the initial crystalline face parallel to the substrate surface. Only later, after becoming older and more massive, do they take to a settled way of life and, obviously, become more or less firmly joined to the substrate. The similarity or even sameness of the structures of the substrate and growing crystal do not, in many cases, lead to strict continuity of the "brickwork". This means that epitaxy is not always directly responsible for facilitating crystallization on the face of a crystal of similar structure. But in these cases easier crystallization can be attributed to the fact that similarity or sameness of the structures leads to an extremely low value of the surface energy at the interface between the substrate and nucleus of the new phase.

Supercooling liquid and the glassy state. The phenomenon of “autoepitaxy” can be graphically demonstrated by a simple, but interesting experiment that anyone can perform. Into a sulphur melt lower a small crystal of monoclinic sulphur on a thread and a small crystal of rhombic sulphur on another thread. Very soon you will see that, notwithstanding the identical conditions they are under, both crystals of different crystalline shape grow simultaneously, though, it may be, at different rates. But if there is no seed crystal in the melt, it may cool below the point of normal crystallization. The point of normal crystallization is a point at which liquid and crystalline sulphur are in equilibrium.

It is even simpler to demonstrate the feasibility of supercooling a liquid by taking hyposulphite, used as a fixative in photography, and, after melting it at a temperature of about 70°C , cooling it to room temperature. It can be kept in this state for a long time.

The crystallization of supercooled liquids is usually prevented by their high viscosity. Such viscosity is inherent in cooled liquids having molecules either of complex composition (all soda-lime glasses) or ones that readily form complex aggregates (quartz molecules). The German physicist and chemist, Gustav Tammann, showed that when the viscosity exceeds a limit of the order of 10^{14} poises, crystallization often becomes practically impossible: any change in the configuration of the molecules is hampered by their low mobility. (A poise is a unit of dynamic viscosity equal to the dynamic viscosity of a fluid in which there is a tangential force of one dyne per square centimetre resisting the flow of two parallel fluid layers past each other when their differential velocity is one centimetre per second per centimetre of separation.)

The property of glass to retain its transparency for

a long time, sometimes for centuries, is due to the phenomenon just explained. Occasionally, however, the transparency of glass is impaired by the formation of fine crystals; this is called devitrification of the glass. In certain cases it proves possible to obtain substances with very simple molecules in a "glassy" state. For example, glasslike, or vitreous, carbon can be obtained under definite conditions.

Glycerine has had some interesting adventures in this field. For a long time nobody could manage to obtain it in the form of crystals. Then a merchant in France found that he had bought glycerine in the form of small crystals from a wholesale dealer. The merchant decided that the purchase was either not glycerine at all or that it was highly polluted. Later on, after heating and melting the glycerine crystals and precisely comparing the liquid with "normal" glycerine, they were found to be identical. The rare phenomena of glycerine crystallization was, in this manner, "discovered". The reason for the crystallization was the shaking and jolting the glycerine had been subject to during shipping over a stormy sea.

Thus, we have looked into, in very simplified form, of course, the theory of new phase formation and the building up of an already existing crystal. But how are these processes implemented in practice in laboratories?

Diamond Synthesis at High Pressures

Equipment for diamond synthesis. Let us begin by agreeing that by high pressure we mean pressures corresponding to the region of diamond stability, and by ultrahigh pressures, those exceeding 500 kilobars, above which the region of diamond metastability again extends. In this region the stable form is metallic

carbon (carbon-3). Here we are dealing with static pressures, i.e. ones at which the specimen is subject to the pressure and temperature for a sufficient length of time, in any case, more than several seconds. Diamond synthesis at high static pressures has become the principal industrial method of producing synthetic diamonds. Dynamic pressures are obtained by compressing a substance by means of shock waves caused, for example, by an explosive. With shock wave techniques, pressure and temperature are applied to the specimen for a very short time, of the order of milliseconds. Dynamic methods of synthesis and investigations of the behaviour of substances at high pressures are being more and more extensively applied in practice, but so far they cannot compete with static methods, though they do complement them.

It is of interest that these two trends in diamond synthesis techniques, the applications of static and dynamic pressures, were laid down by Nature herself. It is a matter of fact that static pressures were once applied in diamond pipes, and dynamic pressures in meteorites.

To produce high pressures it is necessary either to reduce the volume of the specimen being investigated at constant temperature, or to heat it at constant volume. It is still better if we manage to reduce the volume of the substance and to raise its temperature at the same time. All of these operations require special equipment.

Static pressure is produced by powerful presses whose force is transmitted to a high-pressure chamber. A giant hydraulic press exerts a force of tens of thousands of tons on a definite area. The working chamber concentrates this force on an area of several square centimetres. The apparatus, or mechanism, that links the press, exerting the force, to the chamber, concentrating the force in the effective volume, is called

the pressure booster. The ratio of the pressure obtained in the effective volume to that exerted by the press is called the boosting factor. Naturally, the higher the boosting factor, the higher the pressure in the effective zone of the high-pressure chamber. Pressure boosting is something that we continually run into in everyday life: a hand holding a needle is a pressure booster. If you are interested, calculate the pressure obtained at the needle point, 0.1 mm in diameter, if you apply a force of 1 kilogram (or, if you like, even a greater force).

It is impossible to substantially reduce the area of the effective space in the chamber. In the first place, it is difficult to carry out manipulations in an effective zone of very small volume. In the second, even the best materials cannot withstand the excessive loads. If the applied force exceeds the ultimate strength of the material of which the chamber is made, the chamber fails. This circumstance restricts an increase over the design pressures.

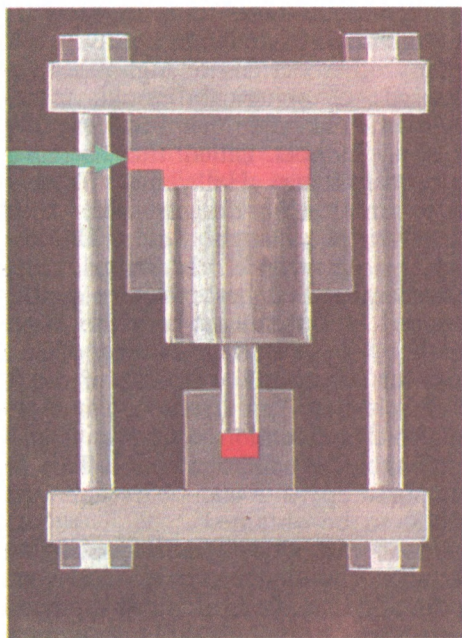
A substantial contribution to the development of high-pressure techniques was made by the American physicist Percy Williams Bridgman of Harvard University; it earned him the Nobel prize in physics in 1946. He did not succeed in synthesizing diamond himself, but, owing to his work, this was achieved by others. It was Bridgman that designed the first version of a high-pressure chamber capable of maintaining high pressures and temperature for a sufficiently long time. His chamber, which was named the "Bridgman anvil", consisted of two symmetrical central parts of cemented carbide with flat anvil faces, these parts being fitted into a hardened steel casing. In 1940 the Bridgman chamber enabled pressures up to 100 kilobars to be reached; this was quite an achievement. But, as is usually the case with a first design version, it had its drawbacks: firstly, a very restricted reaction volume, and secondly,

excessively high heat losses that made it difficult to obtain and maintain high temperatures.

Later, many other designs of high-pressure chamber were proposed: a spherical mould, a tetrahedral chamber with conical guide members, etc. Widely used abroad was a chamber called the "belt" apparatus, designed by H. Tracy Hall and Francis Bundy. A number of interesting designs were developed by scientists and engineers in the Soviet Union. V. P. Butuzov and his co-workers designed a six-piston chamber. A chamber that has extensive application was jointly designed by specialists from the High-Pressure Physics Institute of the USSR Academy of Sciences and the Institute for Ultrahard Materials of the Ukrainian Academy of Sciences. This chamber resembles cuplike anvils into which a reaction container is placed. This container is almost lenticular in shape. This installation enables pressures up to 200 kilobars and temperatures up to 3000 K to be obtained.

The reaction zone is heated by passing an electric current through it, with the anvils serving as contacts. Today, in diamond synthesis, it is not the specimen that is compressed and heated, but the reaction container. This container performs a number of functions. In the first place, it transmits pressure from the anvils to the specimen; in the second, it forms the gasket between the pistons. Upon compression, the material of the container is squeezed out to form the sealing gasket. In the high-pressure chamber equilibrium is set up between the friction force opposing the squeezing-out of the container material and the force pushing it out.

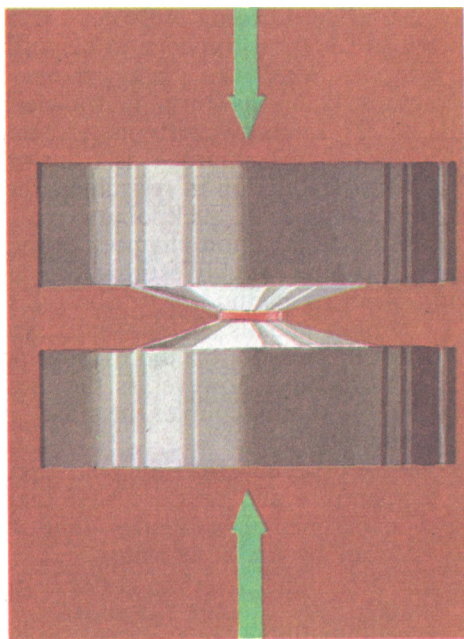
The container material should be a good transmitter of hydrostatic pressure, have low thermal and electrical conductivities, a high melting point, a low compressibility and, as far as possible, not participate in any chemical reaction with the specimens being used.



Schematic diagram of a device for synthesizing diamonds at high pressures. Static pressure is produced by powerful presses; their forces are transmitted to the high-pressure chamber. A hydraulic press develops a force up to tens of thousands of tons applied to a definite area.

In the majority of cases, the container is made of pyrophyllite (pencil stone), lithographic limestone (limestone with an admixture of a highly dispersed clayey component) and talc (hydrated magnesium silicate).

The pressure in the reaction volume is measured by the method of recording phase transitions, using the



The Bridgman anvil was the first design version of a chamber capable of maintaining high pressure and temperature for a length of time. Here two symmetrical pressure components of cemented carbide are mounted in a hardened steel casing.

fact that many properties of substances are drastically changed in a phase transition. This method is based on Bridgman's investigations, which established a relationship between electrical resistance and pressure for many elements and compounds. Bismuth has found wide application in this method because it is transformed into a series of polymorphic modifications,

or polymorphs, when different pressures are applied to it. Thus, bismuth I is transformed into bismuth II at 25 kilobars, with its resistance being reduced by 83 percent; bismuth II, in its turn, is transformed into bismuth III at 27 kilobars, with its resistance being doubled. Finally, when bismuth V is transformed into bismuth VII with a reduction in resistance, the pressure in the reaction chamber is 89 kilobars.

Temperature in the reaction chamber is measured in various ways. It can be roughly estimated by the power consumption. Another method is to observe the fusion (melting) of certain metals (taking into account, of course, the effect of pressure on the melting point). The most widespread method, however, is the measurement of temperature by thermocouples installed inside the reaction chamber itself.

It goes without saying that all the methods for measuring temperature and pressure have many special features and experimental subtleties that should be taken into account by an investigator.

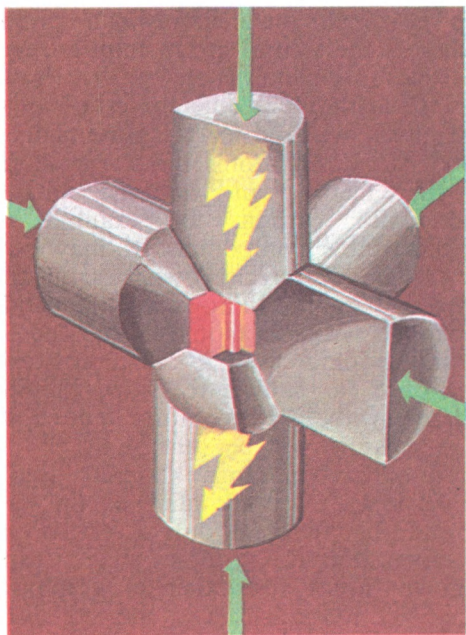
Source material for diamond synthesis. The container is charged with a mixture of graphite and a metal: nickel, iron, manganese, etc. Also employed are alloys of metals, for example, nickel with manganese. The synthesis of diamond begins after melting the metal. The effect of metals on the synthesis has been investigated in great detail, but the question has not yet been fully cleared up. Mainly, metals of the iron group are used with various admixtures. Many patents taken out in various countries are "full", not only with all the chemical elements, but with all possible alloys and intermetallic compounds. The majority of investigators that have assessed the role of metals in synthesis can be divided into two groups. The

first group regards the metal simply as a solvent for the carbon, whereas the second group emphasizes the catalytic properties of the metal. Therefore, one should not be surprised if, in the literature, different terms: solvent metal or catalyst metal, are used for the same metal or alloy.

We speak of carbon atoms dissolved in the metal; actually, the metal can combine into various compounds with carbon, for example, carbides, including metastable compounds. It may be possible that these carbides are precisely what carries the carbon to the growing diamond. In any case, the metal or alloy used in diamond synthesis should be capable of wetting diamond and graphite well; it should dissolve carbon and also have a sufficiently low melting point (otherwise, the synthesis temperature and, consequently, the applied pressure will be very high).

The kind of carbonaceous material used and its dispersity have an essential influence on the rate of synthesis and the diamond output per pressing and sintering operation (i.e. in a single experiment). A well-known Soviet researcher of graphitic carbon materials, V.I. Kosatochkin, showed that the transformation to diamond is affected by the capacity of the carbonaceous material to be graphitized, i.e. to form a structure typical of graphite. If the source material lends itself to graphitization, the process ends sooner and the diamond output is higher than when the carbonaceous material is not capable of being graphitized.

Today, a great many different kinds of carbonaceous materials are known. They include natural graphites, coals, cokes, and synthetic materials: pyrographite, glasslike carbon, etc. Synthetic graphites are obtained either by precipitating them from the gaseous phase in the pyrolysis of hydrocarbons, or by the carbonization



Six-piston chamber for producing high pressures. It was designed by a team of Soviet scientists.

of coal tar at high temperatures. Depending upon the operating conditions: temperature, time and pressure, the materials obtained are of a structure close in various degrees to that of graphite. These materials are differentiated according to their degree of graphitization, i.e. the closeness of their structure to graphite.

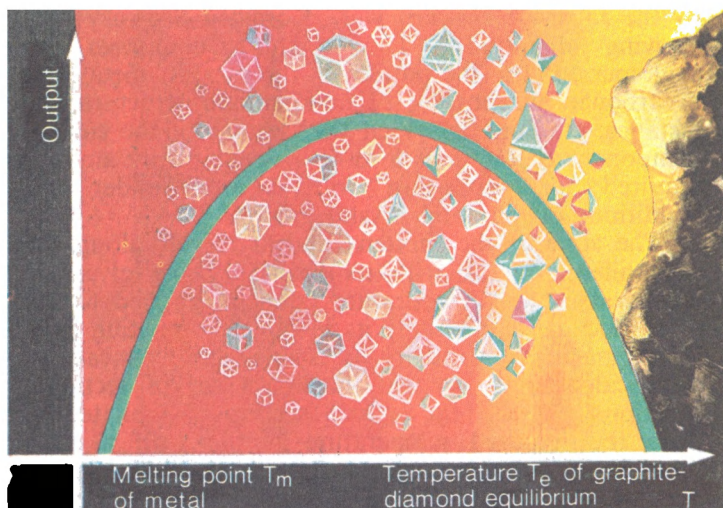
There is an immense number of combinations of metals, alloys and carbonaceous materials. We give, as an example, the composition of the mixture proposed

by the Japanese concern K. K. Komatsu Seiskusyo for growing diamond: "The mixture comprises an agglomerate of a fine powder of the catalyst metal and a carbonaceous powder of nondiamond structure, for instance, graphite, in which the content of the carbon component is less than 6 to 40 percent of the amount required for saturation with carbon under the conditions of diamond crystal growth.

"The zone of the molten catalyst travels along the carboniferous stock with its position being given by means of a local temperature gradient, applied to the stock and travelling along its length. The melting zone is obtained in an ordinary pressure device by means of a helical heating element, having a set of sectional junctions. The current in each section is regulated to form the required temperature profile with a local temperature peak that creates the melting zone, and to provide for travel of the peak along the stock."

Parameters of the synthesis process. Temperature and pressure have a decisive effect in synthesis on the shape of the diamond crystals. At low temperatures, the crystals grown are mainly of cubic shape, at high temperatures they are mainly octahedrons, and at intermediate temperatures, cuboctahedrons*. As we now know, a change in temperature leads to a change in pressure. Hence, we cannot retain the parameters that correspond to the region of diamond stability in the process if we arbitrarily vary the temperature without providing for the necessary pressure. It is a fact that by increasing the temperature we can find ourselves beyond the

* A polyhedron with six equal squares and eight equal equilateral triangles for faces, which can be formed by cutting the corners off a cube. One of the 13 Archimedean solids.



Curve showing the dependence of crystal growth on the temperature. At a low temperature the crystals grown are mainly of cubic shape; at a high temperature, they are mainly octahedrons.

limits of the diamond stability region if we do not increase the pressure simultaneously.

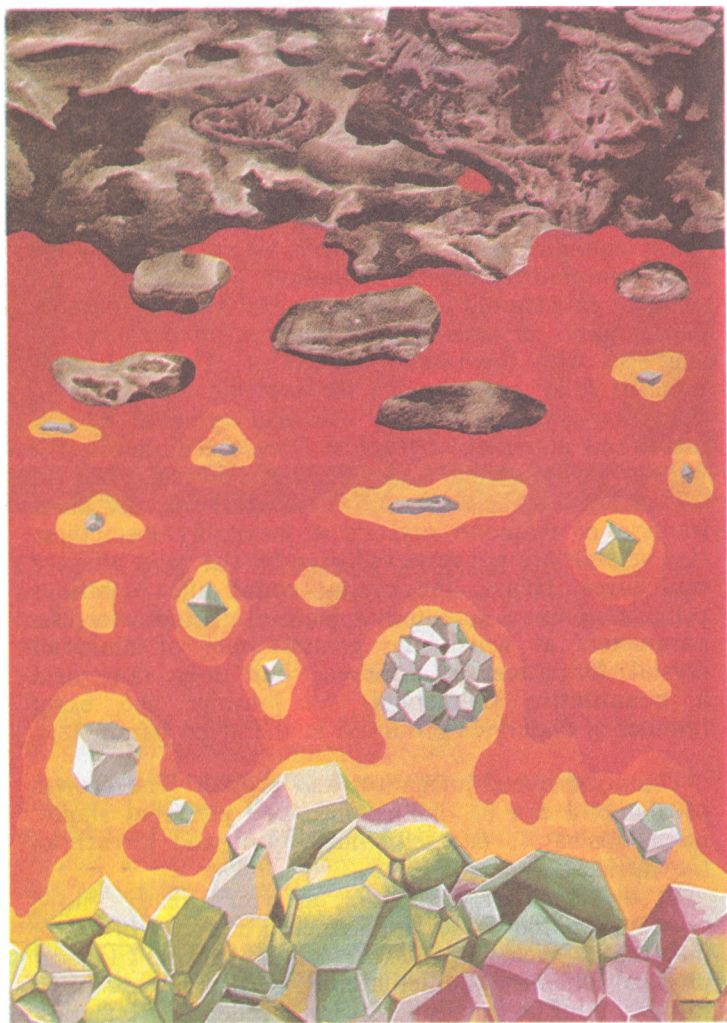
At constant pressure the diamond crystal output depends upon the temperature, and there is a temperature at which the maximum number of crystals are produced after synthesis. The existence of this maximum is readily explained. Assume that the pressure in the reaction zone is maintained constant, and the temperature is raised from zero to the graphite-diamond phase transition point corresponding to the given pressure. Then at temperatures below the metal

melting point, the rate of diamond nucleation is very low, practically equal to zero. The rate of nucleation of diamond crystals is also zero at a temperature corresponding to the curve of the graphite-diamond phase transition. The maximum rate of diamond crystallization is observed at a certain intermediate temperature, above the melting point of the metal but below the temperature at which graphite and diamond are in equilibrium. In other words, we are observing the maximum rate of crystal formation.

Great care should be taken in correlating the number of diamond crystals found after an experiment in synthesis with the rate of nucleation. This is usually done as follows. Following the pressing and sintering operation and subsequent chemical removal of the metal and nonreactive graphite from the diamond, the number of diamond crystals are counted. But in separating out the diamonds after synthesis, the finest fraction of diamond crystals is inevitably lost; these tiny crystals are not retrieved even by the most efficient centrifuges. Hence, the crystal count after synthesis provides only a qualitative picture; it indicates the parameters at which the greatest rate of diamond crystal formation is achieved, but does not yield a quantitative (numerical) relationship: the exact number of diamonds produced at the given parameters.

Diamond nuclei formation and growth. The growth of diamond can be divided into two principal stages: nuclei formation (stage of nucleation) and growth of the nucleated crystal.

In the stage of nucleation, as you already know, critical diamond nuclei are formed, i.e. nuclei of a size that makes them capable of further growth. Classical physical chemistry differentiates two main cases of formation of a new phase: homogeneous nucleation



and heterogeneous nucleation. In homogeneous nucleation the critical nucleus is surrounded on all sides by the crystallizing medium; in heterogeneous nucleation, the nucleus is formed on the surface of some foreign body.

Let us now compare these two cases of nucleation.

If we take a mixture of graphite and metal powders and bring it to the state corresponding to the region of diamond stability, with the metal in the molten state, the rate of homogeneous nucleation will be negligibly low. This is mainly due to the extremely high surface energy at the diamond-metal interface.

An estimate of the rate of heterogeneous nucleation yields much more attractive values and, consequently, diamond begins to crystallize on some kinds of foreign surfaces. As a matter of fact, inclusions of graphite and metal carbides are observed in many synthetic diamonds. Frequently, natural diamonds also contain inclusions of associated minerals.

Let us consider an interesting hypothesis advanced by Ya. A. Kalashnikov, a researcher on the staff of L. F. Vereshchagin, member of the USSR Academy of Sciences. This hypothesis is a sort of hybrid of the solvent and catalyst ideas. Graphite can dissolve in metal in the form of fine lumps, or blocks, so that a colloidal solution is obtained. The large particles of graphite gradually dissolve if they are given enough time. Following a sufficiently long holding time, they completely disappear, forming a true solution of carbon in molten metal. But the diamond synthesis process is measured in seconds and minutes; during this time graphite particles of colloidal size are still retained.

Kalashnikov next assumes that the metal atoms pass

Formation and growth of diamond crystals in molten metal subject to static pressure.

(diffuse) between latticed planes (one atom in thickness) in the graphite, break down the graphite-type bonds and convert them into diamond bonds. In other words we have a sort of needle and thread joining the latticed planes of the graphite into a diamond crystal.

But this is not the only feasible transformation mechanism. The authors of the present book have shown that particles of graphite of definite shape can be transformed into diamond by themselves, because their existence as diamond is thermodynamically more favourable, i.e. the state in the form of diamond has less energy. Therefore, the mechanism for the very initial stage of diamond formation at high pressures can be pictured as follows.

Graphite particles of various shapes go into solution in the molten metal. Certain of them can possibly be converted into diamond, and such a conversion takes place. These diamond nuclei continue to grow, and the graphite particles that were not thus converted dissolve.

The dissolved carbon supplies material to the growing diamond. Such a theory explains the role of the metals, employed in diamond synthesis, as solvents and as catalysts of a certain kind (because they do accelerate the chemical process). As a matter of fact, for a diamond nucleus to be formed, the graphite particles must go into solution. This makes the metal a solvent. Holding most promise for synthesis, however, are the metals at whose interface the surface energy of diamond is minimal. This facilitates diamond formation, and such action of the metal can be conditionally called catalytic.

At the same time, this approach enables the necessary properties to be specified for the graphitic materials that are to be used in diamond synthesis. Obviously, the graphitic material should already contain the particles that are capable of being

transformed into diamond, i.e. it must have a definite structure. A whole group of graphitic carbon materials is available that readily dissolve in molten metals, but, not having a crystalline structure, are incapable of producing diamond in synthesis. Primarily, such materials include certain kinds of glasslike carbon and carbon black.

Assume that in one or another manner a critical diamond nucleus is formed, and that it is capable (under proper conditions!) of further growth. The tiny crystal is going to grow in a supersaturated (with respect to diamond) medium, attaching atoms (and, perhaps, whole blocks) of graphitic carbon. Research has shown that at the initial instant the rate of diamond growth is very high and may reach 60 micrometres per second. Then the growth rate drops. Diamond crystals of different shapes have different rates of growth under the same conditions. The maximum initial rate of linear growth is observed for cuboctahedrons.

Kinetic and diffusive regions of the process. The process of crystal growth proceeds as if it were divided into two operations: delivery of the building material to the site and incorporating it into the crystal. If the rate of delivery of carbon atoms to the surface of the diamond is high, its growth depends mainly on the second operation, i.e. the rate at which the carbon is built into the diamond lattice. This kind of process takes place in the kinetic region. If, however, the carbon is very rapidly built into the lattice, whereas its delivery to the surface of the crystal, taking place due to diffusion, runs into difficulties, then the rate of diamond growth is determined by the slowest (limiting) stage: diffusion. Such a process takes place in the diffusive region. In the second process, a zone depleted

in carbon is formed around the growing crystal. Such a zone can be observed in photographs. The depleted zone is called the "crystallization courtyard".

The whole process of diamond crystal growth can be roughly pictured as follows. The graphite and diamond are separated by a layer of metal. In the region of diamond stability, the concentration of carbon in the liquid metal in equilibrium with graphite is higher than the concentration in equilibrium with diamond. Therefore, in this region, the graphite can dissolve and the diamond can grow. Carbon atoms of the graphite pass by diffusion through the layer of metal and precipitate on the diamond.

If only a small number of crystals are formed in the stage of nucleation, if their growth rate is low and they do not interfere with the growth of one another, individual well-faceted diamond crystals are obtained. But if crystals are formed that grow at a high rate, they have, as a rule, a very defective structure. The formation of defective crystals is due, not only to a high growth rate, but also to the substantial inequalities in the temperatures and in the pressures at various points throughout the volume of practicable synthesization chambers. One can hardly expect to obtain a diamond that is perfect with respect to its faceting and internal properties if the temperature along it varies by several hundreds of degrees. Sometimes so many nuclei are formed that the crystals intergrow with one another, forming a continuous plate with protruding vertices of individual crystals, a so-called druse. Of interest is the fact that crystals of druses are always well faceted because their growth rate is low.

There is a general law of diamond growth: the higher the temperature, the faster synthesis is completed and the smaller, more defective and more poorly faceted are the diamond crystals obtained. But, all other things

being equal, the diamond output per pressing and sintering operation is higher.

Industry needs a great variety of different kinds of diamonds, and diamonds are synthesized, therefore, under a great variety of conditions.

But where are the large diamonds? This, without doubt, is a question that every reader surely asks sooner or later. Why make a secret of the fact that practically everybody, when they hear or read the word "diamond", visualizes a gemstone, a crystal that must be, not only large, but of jewel quality, transparent and free of inclusions or flaws. At the present time diamond synthesis techniques have made available the possibility of producing such crystals. Such an experiment was conducted by Herbert Strong in a chamber of the belt type. A layer of metal was arranged in the container above the seed diamond. The source of carbon was also diamond or, to be more exact, diamond powder. The temperature of the powder exceeded that of the seed crystal by 50 degrees and this difference was maintained to an accuracy of one degree. The process took several hundred hours and resulted in the production of well-faceted crystals of gem quality up to 0.6 carat in weight. But their cost was so much higher than that of similar natural diamonds that the application of this method in practice is absolutely out of the question. This, possibly, is the reason why this method of synthesizing diamond crystals was not patented and only a journal article reported on Strong's experiments.

The problem of large crystals is, in essence, the problem of the size of the high-pressure chamber. A crystal obviously cannot become larger than the vessel in which it is grown. On the contrary, the size of the crystallization volume must considerably exceed the

expected size of the diamond crystal. But the larger the crystallization chamber, the more difficult it is to provide in it the required pressures and temperatures. It is even more complicated to maintain the parameters of the process constant. This is impeded by the diamond synthesis itself. One reason is that the density of diamond is 3.5 g/cm^3 and that of the graphite used in synthesis is, at best, 1.8 to 2.0 g/cm^3 . This means that practically a single volume of diamond is formed in place of two volumes of graphite. Moreover, the electrical properties of the reaction zone are changed because of the transition of current-conducting graphite to nonconducting diamond.

As is evident, difficulties encountered in developing a commercial process of producing large monocrystals of diamond are enough and to spare. It is necessary to take into consideration the complexities of this problem. There is perhaps no reason to make exceptional efforts to solve it; at present large polycrystalline synthetic diamonds are being produced that have succeeded in efficiently replacing even natural diamond in many fields.

Diamond and an explosion. We have described diamond synthesis in the presence of metals at static pressures. But, as mentioned earlier, methods are being developed today for obtaining diamond by means of dynamic pressures due to impact loads. The crystallization chamber in this case is a thick-walled cylinder with a movable piston above which the explosive charge is arranged. Under the piston is a layer of graphite held in a special cup. Following the explosion a shock wave propagates through the graphite. During a length of time from 3 to 6 milliseconds, the graphite is subject to a pressure up to 150 kilobars and a temperature of 2500°C . Direct transition of part

of the graphite into diamond takes place. Along with ordinary cubic diamond, its hexagonal modification, lonsdaleite, is also formed. This latter, as we have indicated above, is also found in meteorites.

Now we know how diamond is obtained at high pressure, i.e. in the region of its stability. This raises the question: is diamond synthesis feasible in the region of graphite stability?

Diamond Powder Growth at Low Pressures

Essence of the process. Diamond growth is possible in the region of pressures and temperatures in which it becomes the less stable form of carbon, and graphite is the stable form. This is said to be diamond production at low pressures. A low pressure may be hundreds of atmospheres or a fraction of an atmosphere. The problem is to make the appearance of a diamond nucleus and its further growth more probable by properly selecting the conditions under which the experiment is to be conducted.

The probability of diamond growth is substantially increased if a diamond seed crystal is available. In a proper hydrocarbon medium, for example in methane, the following decomposition reaction proceeds on the surface of the seed diamond:



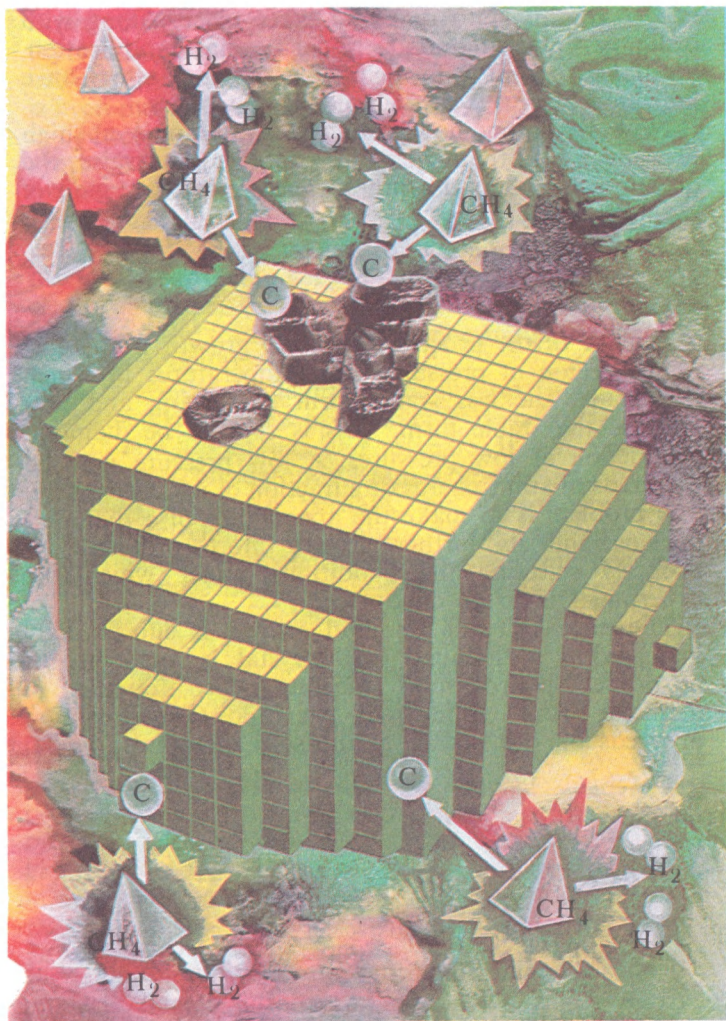
Diamond

or



Graphite

For an equilibrium concentration, the number of carbon atoms being attached to the crystal and the



number leaving it are equal, so that the crystal is simultaneously growing and being decreased, with the total rate of growth equal to zero. If the carbon atom concentration is higher than the equilibrium value, surplus atoms (in comparison with the equilibrium concentration) are deposited on the faces of the crystal. Owing to "autoepitaxy" these atoms tend to continue the "bricklaying" sequence of the substrate. But if the carbon atom concentration near the crystal is too high and the process of their deposition on the face of the seed crystal is too rapid, the formation and growth of graphite, a thermodynamically more stable form of carbon, become possible. This outweighs the influence of "autoepitaxy". At the beginning the formation of graphite and growth of diamond proceed simultaneously at different parts of the surface, but then graphite covers the whole surface of the crystal and diamond growth ceases.

Thermodynamic calculations indicate that the equilibrium concentration of carbon in chemical compounds, in a vapour or a solution above diamond at low pressures, is higher than that above graphite. Therefore, there is always a probability of graphite deposit, which closes off the surface of the diamond and prevents its further growth. The primary difficulty of diamond growth at low pressures is to avoid the deposit of or to get rid of the overgrowth of graphite, this stable phase of carbon. This is done in various ways. Synthesis can be periodically interrupted to remove the graphite in some manner from the surfaces of the diamond crystals. It is possible to select conditions of synthesis in which the rate of diamond

Diamond growth from the gaseous phase at low pressures. Methane disintegrates; diamond is built up on the surfaces of the crystal (*below*), as well as graphite (*above*).

growth is so much higher than that of graphite growth that inclusions of graphite are “walled up” within the layers of diamond. Finally, we can attempt to devise a synthesis technique in which no graphite at all is formed.

It is an intriguing idea to increase the size of diamond crystals in the proper carbonaceous medium. The first attempt to conduct such an experiment took place at the turn of the century. Today, patents and papers in scientific journals concerning this problem are appearing more and more frequently in various countries.

In 1956, two scientists from the Physical Chemistry Institute of the USSR Academy of Sciences, B.V. Derjaguin (one of the authors of the present book) and B.V. Spitsyn, were the first to patent a method for building-up diamond seed crystals from a gas. In their experiments they made use of carbon tetrabromide (CBr_4).

Somewhat later (1958), two patents for the buildup of diamond powder were obtained by the American scientist William G. Eversole. The first deals with diamond growth from hydrocarbons containing methyl groups, and the second, with diamond growth in decomposing carbon oxides. Since graphite also grows, together with diamond, Eversole interrupted the process periodically and removed the graphite by pickling in a hydrogen medium at 100 atm and 1000°C.

Equipment and procedure for building-up diamond powders. A group of researchers, headed by B.V. Derjaguin and D.V. Fedoseev, conducted theoretical and experimental investigations in diamond synthesis from gases, trying to gain an insight into the diamond and graphite growth mechanisms. From the very beginning, two aims—pure research and its industrial application—were closely interwoven.

First of all, the experimenters cleared up the dependence of the rate of diamond growth (and, at the same time, graphite growth) on such parameters as temperature and pressure of the carbonaceous gases.

The experiments were performed in laboratory installations consisting of a synthesis reactor and a vacuum system. The reactor, usually of cylindrical shape, is made of quartz and can withstand a temperature up to 1200°C . It is inside a furnace, which is made of wire or strip of a special alloy. With an electric current the strip becomes hot and heats the reactor. The temperature of the reactor is measured by several thermocouples located in a special quartz pocket.

The vacuum system includes vacuum pumps, gas cleaning and storage unit, a number of pressure gauges of various kinds for measuring gas pressure in a wide range, and a gas flowmeter.

The diamond powder is first weighed and then put into a small quartz cup and inside the reactor. In the first installations for investigating diamond growth kinetics, about 0.1 carat, i.e. 20 milligrams of powder, was used. The cup containing the diamond powder was suspended by a thin quartz thread from a calibrated spring made of a quartz helix. The helix was in the cold zone of the reactor, and the cup with diamond powder, in the hot zone. A special scratch marked on the end of the helix could be observed in a small microscope with graduations, so that any changes in the weight of the specimen of diamond dust could be measured in millionths of a gram.

Highly dispersed (finely pulverized) diamond powders were employed in all measurements associated with investigations of diamond growth kinetics. Such powders have a large specific surface, i.e. the total

surface of all the particles in one gram of powder. The smaller the size of the particles, the greater the specific surface. This you can easily see for yourself by assuming that you are consecutively dividing an initial cube with edges 1 cm long into smaller and smaller cubes.

Assume that in the process of buildup we obtain a diamond layer 10 angstroms thick. If we take a single small diamond crystal weighing 20 milligrams, it will be a cube with an edge about 4 mm long and a total surface area of about 1 cm². How much is the obtained increase in weight of diamond equal to in this case? Knowing as we do the density of diamond we can readily find that the increase in weight is equal to 0.35×10^{-3} milligrams. Such an increase in weight is beyond the limits of sensitivity of the scales we have selected.

Next we take the same 20 milligrams of diamond, but in the form of a powder with such fine particles that its specific surface is equal to 10 square metres per gram of diamond. Then the total surface area of powder on which diamond growth can proceed is 0.2 m² and the increase in weight comes to 0.7 milligrams, which is much greater than the sensitivity of the scales. Thus, for the given increase in diamond weight we can measure its rate of growth.

Specific surface. This is one of the most important characteristics of powdered materials, and not without reason is it specified in all government stand-

Reactor for building up diamond powders. The installation consists of the reactor proper and the vacuum system. The reactor can withstand a temperature of 1200°C.

Reactor for building
up diamond powders

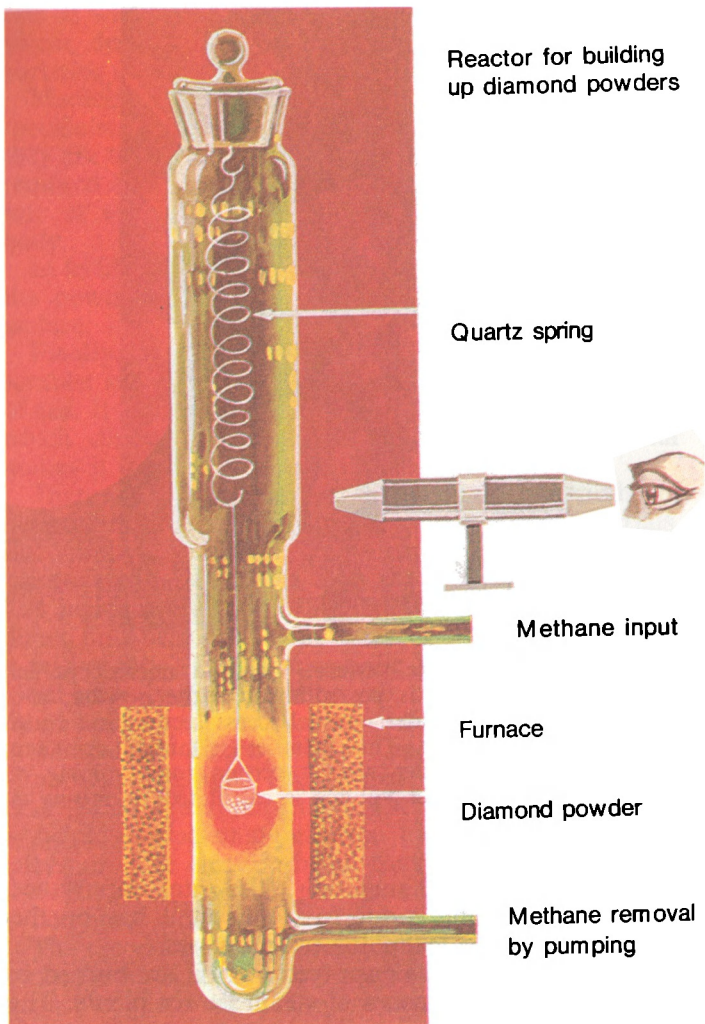
Quartz spring

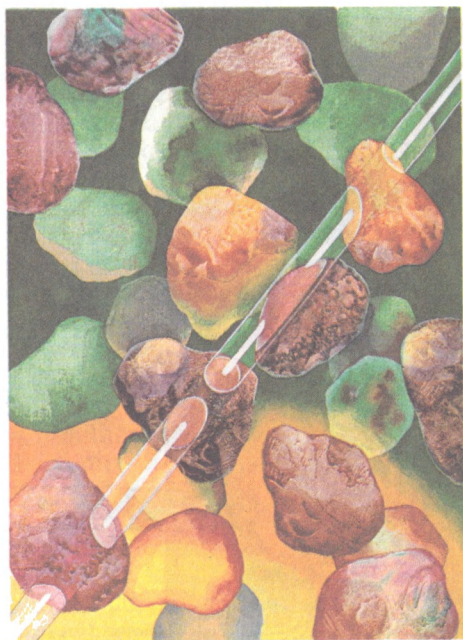
Methane input

Furnace

Diamond powder

Methane removal
by pumping





Determining the specific surface. Under a microscope an imaginary straight line is passed through the powder, and then an imaginary cylinder of small cross section is formed about the straight line. This cylinder seemingly cuts out a column of the powder with a certain total volume of particles of powder. This volume is calculated by means of special equations.

ards for all powdered materials. The vital importance of this characteristic is due to the effect it has on the efficiency of many technological processes.

Finely crushed coal or sprayed fuel oil are burned in the fireboxes and furnaces of steam power plants. The

rate at which energy is evolved in combustion in these plants depends substantially on the size of the coal particles or fuel oil droplets, i.e. their specific surface.

Medicines are also dried to powders with a given specific surface. Many medicines are made so that after they are taken they disintegrate into a powder with the required specific surface. This enables regulation of the rate at which the medicine becomes available in the body.

In fertilizing fields, especially with the aid of aviation, the powdered fertilizer also has the required specific surface.

Finally, just observe how instant (immediately soluble) sugar behaves when you put a cube in a glass of tea. It first disintegrates into separate small crystals which dissolve independently. This, in fact, is what makes it readily soluble.

There are, of course, a great many methods of determining the specific surface of powdered materials. But, notwithstanding the seeming diversity, these methods can be divided into three main groups. The first includes methods of finding the specific surface by direct measurement of the sizes of the particles under a microscope. Then the specific surface is calculated. Until recently this operation was carried out practically by hand. A laboratory assistant made the measurements directly under the microscope or from a photomicrograph. Today, instruments are available that do this automatically. They are based on the principle of a scanning electron beam like that used in television. The electron beam runs along the surface of the plate on which the powder is applied and a computer counts its reflections from the particles.

The second group of methods for measuring specific surface is associated with the adsorption of gases by the surface of materials. These are the so-called adsorption

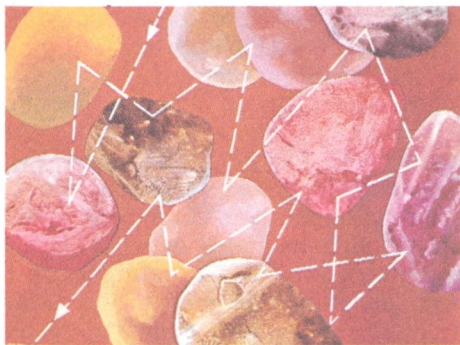


Internal and transport pores in a powder (under a microscope).

techniques. The adsorption phenomenon consists in the adherence of gas molecules to a surface. This principle is the basis for the protective action of a gas mask, which contains a layer of activated charcoal. Such charcoal always has a large specific surface. The particles of activated charcoal are relatively large, up to several millimetres in size. But, owing to special treatment, they have large internal porosity in the form of communicating channels.

Thus, even for a small external specific surface, determined by the geometrical dimensions of the particles, they have a large internal specific surface due to the well-developed internal porosity. For example, ordinary activated charcoal has a specific surface of 500 m^2 per gram. Twenty grams of such charcoal has a total surface area equal to one hectare ($10\,000 \text{ m}^2$ or almost 2.5 acres).

A gas molecule, adhering to a surface, occupies a definite area. If in a closed volume we measure the pressure of a gas and then put the powder in this



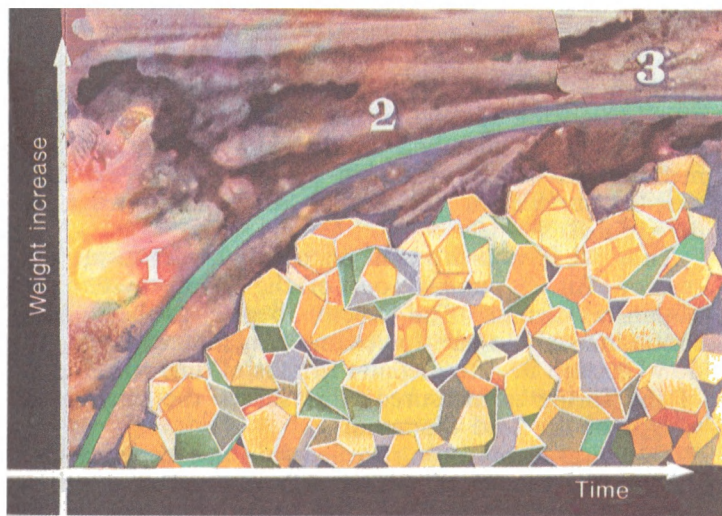
Paths of the molecules in the diffusion of a powder (under a microscope).

volume, the pressure changes because a part of the gas molecules settle on the surface of the powder. Since we know the change in pressure in the system, the amount of powder put into the vessel and the area occupied by one molecule on the surface, we can readily determine the total surface of the powder and its specific surface.

Adsorption techniques yield the value of the total specific surface, internal and external. In many cases, however, it is only the external specific surface that is required; it depends upon the size of the powder grains. Adsorption methods are not at all suitable for measuring only the external specific surface when the powder has internal porosity of its particles. In a very large number of important problems in regular practice, the properties of materials depend on the grain or particle size. An example is abrasive powders, including diamond powders, used in grinding and other machining operations on various materials. Powders like cement, metal powders for powder metallurgy, and powdered dyes require in their characteristics only the external specific surface.

Most of the methods for measuring the external specific surface of powders are based on the resistance which a column of the powder offers to the passage of a gas or liquid through it. The use of the flow of a liquid, for instance, water, is less expedient, because it can be complicated by the solubility of the particles and other matters associated with their interaction with a liquid. The resistance of a column of powder to the flow of gas through its pores depends, in the general case, in a complex way on the ratio of the mean free path of the gas molecules (from one collision with another molecule to the next collision) to the average clear opening in the pores. The law of gas flow is simplified in the limiting case when this ratio becomes much larger than unity. This simplification occurs because, in this case, the gas molecules collide with one another much less frequently than with the walls of the pores.

In this way, the various molecules of the gas travel mainly independently of one another, and the kinks and sharp bends in their paths are determined only by collisions with the pore walls. The path of the molecules is a broken, zigzag line. In this respect, it resembles the chaotic random motion of molecules of a dissolved substance colliding with the surrounding molecules of the solvent. The disorderly motion itself is a manifestation of thermal motion, whose average energy, as we know from physics, increases proportionally to the square root of the absolute temperature. Such random motion of the dissolved molecules, in cases when their concentration is nonuniform in the solution, leads to mass transfer from a region with greater concentration to one with less concentration. Owing to the random motion of the molecules, the scent of perfume, spilled at one end of a room, will spread, after a length of time, throughout



Diamond powder buildup curve.

the room. Here the air is the solvent and the molecules (quite large and complex) of the fragrant perfume are transported.

If we consider the diffusion of gas molecules through the particles of a powder, when the pressure is so low that the molecules do not practically collide with one another, but only with the surface of the particles, we can determine the resistance to diffusion. The coarser the powder, the greater the clearances between the particles and the easier mass transport through the powder. This problem of the resistance of a layer of powder was rigorously solved by B. V. Derjaguin, who found a dependence between the resistance of the powder layer and the size of the powder particles. A number of instruments, based on this principle, are

finding extensive use in industry. In these instruments the velocity of mass transfer in the flow of a gas through a powder layer is measured by simple means, after which the specific surface is calculated.

In the case of diamond buildup from a carbonaceous medium, to which we return again, first the external specific surface of the initial diamond powder is determined.

Thus, we have a cup with diamond powder inside the reactor. Air is pumped out of the whole system to obtain a vacuum. The reactor begins to heat and, simultaneously, a gas, for example, methane, begins to flow through it. After definite lengths of time the stretch of the spring is measured; this shows the change in weight of the seed diamond.

One vital feature was revealed by these experiments: the rate of growth of diamond from hydrocarbons is several times greater than that of graphite under the same conditions. With respect to the rate at which carbon is given off by the gaseous phase, the whole process of growth can be divided arbitrarily into three stages. First, practically only diamond grows and the rate of carbon that is given off is maximal. Next the rate decreases somewhat because, along with diamond, graphite also begins to form and grow. Finally, this rate decreases to the value typical for the rate of graphite growth.

The results of the experiment can be pictured in the form of a curve plotted in weight increases vs time coordinates. We obtain a curve emerging from the origin of coordinates and having its convex side upward. If the rate of graphite growth was equal to that of diamond growth, the experimental points would lie on a straight line when plotted. If the rate of graphite growth exceeded that of diamond growth, the curve would have its convex side downward.

Numerous experiments enabled the dependence of the rate of diamond growth on the temperature and pressure to be established. This was done first for methane and subsequently for other hydrocarbons: ethane, propane, ethylene and acetylene. The experiments were conducted in a special installation, in which the furnace, made of graphite, permitted a temperature up to 2000°C. The experiments showed that diamond can grow at temperatures up to 1700° or 1800°C as well.

Since, along with diamond growth in a gaseous medium, graphite is also deposited on the seed crystals, the problem of cleaning the graphite off the obtained powder arose. It is of no use, of course, to grow a thick layer of graphite on diamond and then have to clean it off. It proves expedient to get rid of the graphite before it completely covers the surface of the seed crystals of diamond.

Investigations conducted in the Physical Chemistry Institute showed that the rates of gasification of diamond and graphite with oxygen from the air (rates of oxidation) differ, the rate of graphite oxidation being much higher. This enabled a method to be developed for removing the graphite from the seed crystals of diamond by oxidation in an air stream. It is no longer necessary to transfer the grown powder for cleaning from the reactor to an autoclave containing hydrogen and, after removing the graphite, to transfer it back again. The whole process of growing and cleaning is now carried out in a single reactor. The method is called a cyclic one. It was soon patented in other countries.

Using the cyclic method we were able to build up the initial amount of 4.4 carats (880 mg) of powder by 61 percent in 30 cycles of growth and graphite removal (1.5 hours each). By way of comparison we point out

that Eversole obtained approximately the same weight increase for a similar powder in 85 cycles of growth and graphite removal (each cycle being over 6 hours long).

Kinetic region of diamond growth. Painstaking investigations enabled scientists from the Physical Chemistry Institute of the USSR Academy of Sciences to develop a mathematical theory for the process of joint growth of diamond and graphite. The theory excellently explains the experimental data and is confirmed by them. This theory is also confirmed by the work of American specialists in the field of diamond synthesis from the gaseous phase.

The theory was evolved for investigations conducted under conditions of practically the same concentration of the initial methane throughout the whole layer of powder being built up. But in the buildup of large amounts of diamond powder, this condition may be violated. This happens because, on the basis of design considerations, it becomes necessary to increase the thickness of the layer of diamond powder.

The rate of methane decomposition is proportional to the surface. Therefore, the greater the specific surface of the diamond powder, the higher the consumption of methane that penetrates into the layer of powder. But, if the layer is so thin that the concentration of methane is practically the same, notwithstanding its decomposition, throughout the layer, the rate of diamond growth is determined by the rate of methane decomposition, which is a kinetic factor. This indicates that the process proceeds in the kinetic region.

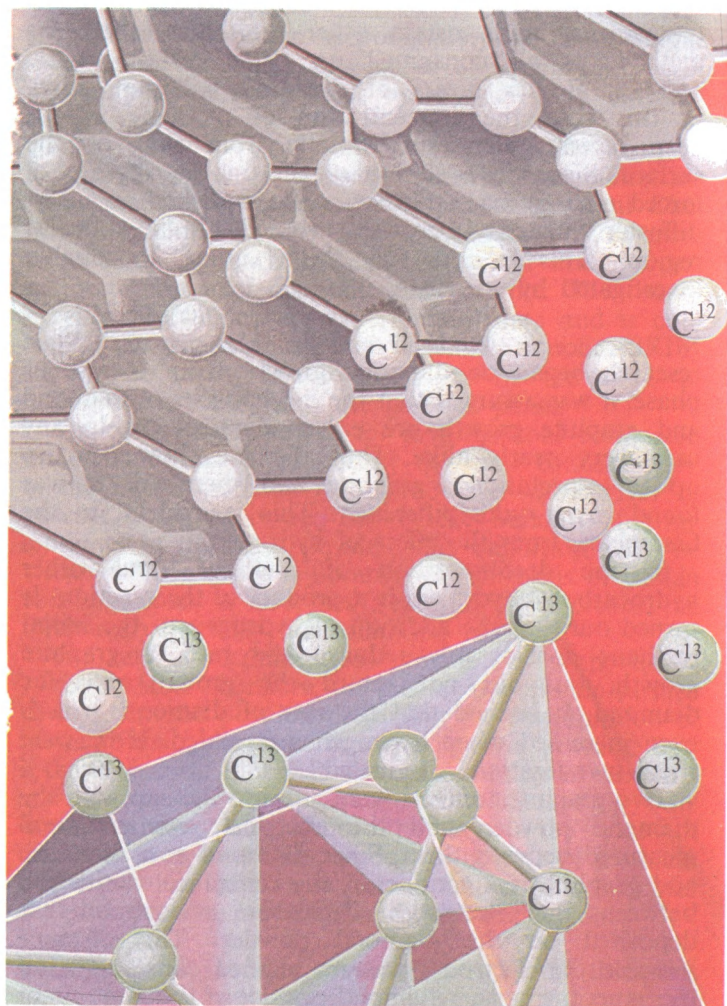
Diffusive region of diamond growth. If the thickness of the powder layer exceeds the limiting value, which depends upon the dispersity of the powder, reaction

temperature and certain other quantities, then the methane is all consumed up to a certain depth, and the deeper layers of diamond will not grow. In this case, the concentration of methane in the deep layers differs substantially from that at the surface. Since, in a stationary gas (in the absence of forced mixing) mass transfer is accomplished owing to diffusion, diamond growth proceeds in a diffusive region. This region has been quite thoroughly investigated by scientists.

Difference in diamond and graphite growth. When research began on diamond growth from a gaseous phase, it was assumed that the mechanisms of diamond and graphite growth are either identical or, in any case, very nearly alike. They did not, however, live up to expectations: graphite and diamond, it was found, grow quite differently. This is evident, in the first place, from the effect of hydrogen.

In the decomposition of methane (and other hydrocarbons) hydrogen is a product of the reaction. It turned out that the addition of hydrogen to the initial methane considerably reduced the rate of graphite growth, but did not retard the growth rate for diamond. It seemed that the rate of diamond growth even increased when hydrogen was added. How were these investigations conducted?

Two graphite contacts were put into the cup with the diamond powder, and the electrical resistance was measured between them. Since diamond is a dielectric and graphite is a conductor, the resistance of the gap between the electrodes decreases as graphite is deposited on the diamond powder. The distance between the electrodes was maintained constant in all the experiments and diamond powder of the same grain size was used. This means that the conductivity



depended only on the amount of deposited graphite. After each experiment the powder was weighed. Then, after removing the graphite, the amount of grown diamond could be determined.

Under definite conditions, in diluting the methane with hydrogen, the amount of deposited graphite decreased, and that of diamond increased. Even the total gain in weight of the diamond seed powder, diamond and graphite taken together, increased. This seemed to be a violation of Le Chatelier's principle, according to which the addition of a product of a reaction slows down the reaction. No fear, however; the principle remained inviolable. Actually, when hydrogen is added, the rates of growth of both diamond and graphite are retarded. The blocking of the surface of the seed particles by graphite is reduced. But, since the rate of diamond growth from hydrocarbons considerably exceeds that of graphite growth, and the share of the surface on which diamond can grow is increased, the over-all rate of its growth is also increased.

The difference in the growth mechanisms for diamond and graphite was especially striking in the fractionation (separation of a mixture in stages) of stable isotopes of carbon.

Carbon has two stable isotopes with atomic weights of 12 and 13, denoted by C^{12} and C^{13} . Geochemical research has shown that in nature all carbonaceous minerals (including graphite and diamond) contain these two isotopes in a definite ratio. Natural diamond is isotopically "heavier" than natural graphite, i.e. it contains relatively more of the heavy isotope C^{13} .

Difference in the growth of diamond and graphite from the gaseous phase. Upon simultaneous crystallization diamond is found to have a relatively greater amount of the carbon isotope C^{13} , and graphite, of the carbon isotope C^{12} .

Moreover, the diamonds in kimberlite pipes are isotopically heavier than the carbonates of the surrounding rock.

Diamond synthesized by high-pressure methods inherits the isotopic composition of the graphite used for the synthesis. When grown from methane, diamond becomes isotopically "heavier" than the growing graphite. Diamond selects from the methane (which also has a definite ratio between C^{12} and C^{13}) more of the heavier isotope of carbon, whereas the graphite makes use mainly of the light isotope.

It is quite natural to link these effects concerning the individual approach of diamond and graphite to isotope selection with the different growth mechanisms of these forms of carbon.

Interesting phenomena are observed in investigating the growth of diamond from various mixtures of hydrocarbons. The rate of growth of graphite from a mixture of methane at a pressure of 0.1 mm of mercury column (0.1 mm Hg) and ethane at the same pressure is equal to the sum of the rates of growth of graphite from the separate gases at the same pressure. But the growth rate of diamond from the same mixture is less than the sum of the rates of growth from the separate components at the same partial pressures.

This is also due to the different mechanisms of growth for diamond and graphite.

It can be supposed that the graphite grows in flat layers, parallel to the seeding surface, from hydrocarbon molecules located on the surface; these molecules had entered the growth region from the gaseous phase. The greater the degree of covering of the surface by hydrocarbon molecules, the more intensive graphite growth. Graphite can be formed only from a large number of molecules of methane (or other hydrocarbon), located directly on the surface. But the

larger the part of the surface occupied by hydrogen, the less there will be hydrocarbon molecules there. Diamond, however, grows only on the part of the surface of a seed crystal that is free of hydrocarbon molecules. But it can also be formed on a surface covered by hydrogen atoms. Therefore, the dilution, for example, of methane with hydrogen accelerates the rate of diamond growth and reduces the rate of graphite growth.

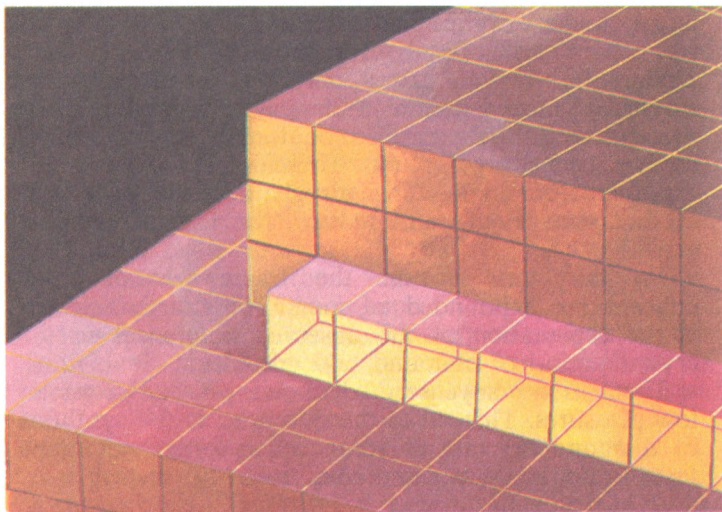
To be found within the framework of these conceptions (expounded, of course, only schematically) is the explanation of the observed differences in the crystallization of diamond and graphite.

Thus, as we have seen, diamond powder grows at low pressures. This raises the question: is the synthesis of diamond crystals of some other form and shape feasible under these same conditions?

Growth of Diamond Films and Crystals at Low Pressures

Production of diamond films. One of the first patented methods of synthesizing diamond films with the participation of chemical reactions included the application of electronic preheating. A carbonaceous gas was passed over the substrate. A special device (quite close in design to what we have in electron-beam tubes that are used in TV sets) produced an electron beam that scanned the surface of the substrate. The beam heated the substrate at the point of contact (this is called local heating). The electron beam passed many times over the surface of the substrate and, as a result, a thin film of diamond was formed.

Information is available on the growing of diamond films from a stream of carbon atoms. In one of these



The surface of a synthesized diamond upon strong magnification under a microscope. Diamond begins to grow only at certain places, rather than over the whole surface.

techniques, the graphite is heated to 4000°C . At this temperature it begins to evaporate and the carbon atoms of the graphite are deposited on the diamond seed bed. Investigators also succeeded in obtaining diamond films from a stream of carbon atoms generated by a carbon arc. In this case electric and magnetic fields are set up between the substrate and source of carbon atoms. This technique can be applied to synthesize diamond films on practically any surfaces.

In the Physical Chemistry Institute of the USSR Academy of Sciences, diamond films were first grown on crystals in the same way as the buildup of diamond

powders. Scores of experiments had to be conducted by D. V. Fedoseev, B. V. Spitsyn and V. P. Varnin to establish whether there really was a weight increase of new diamond. The builtup diamonds (or rather their surface) were investigated by a transmission electron microscope. At the energies applied in such microscopes the electrons cannot pass through thick specimens. This thickness should not exceed a thousand angstroms, whereas the diamond crystals used in the experiments had thicknesses up to several millimetres. To investigate the crystals it was necessary to prepare so-called replicas. For this purpose a thin collodion film was applied to the surface. When the collodion solidifies it is removed to obtain a first-stage replica. Where the diamond crystal had a projection, the replica had a depression, and vice versa.

But the collodion replica began to run when it was heated; the electron beam of the microscope burned through it. To avoid this a thin layer of graphite was sprayed onto the first replica. After dissolving the collodion in a suitable solvent, the graphite film, a second-stage replica, was placed into the specimen holder of the electron microscope and investigated. Owing to the different degrees of electron absorption by various thicknesses, the image produced on the fluorescent screen of the microscope corresponds to the surface structure of the specimen being viewed. In the given case this specimen was the second-stage replica. We deal here with a direct analogy of photography, except that the replica itself plays the role of the negative film.

Investigations showed that diamond first grows only at certain places rather than over the whole surface of the seed crystal. In general, nuclei of a new phase are formed at the parts of the surface that are more active chemically. These are, for instance, various kinds of

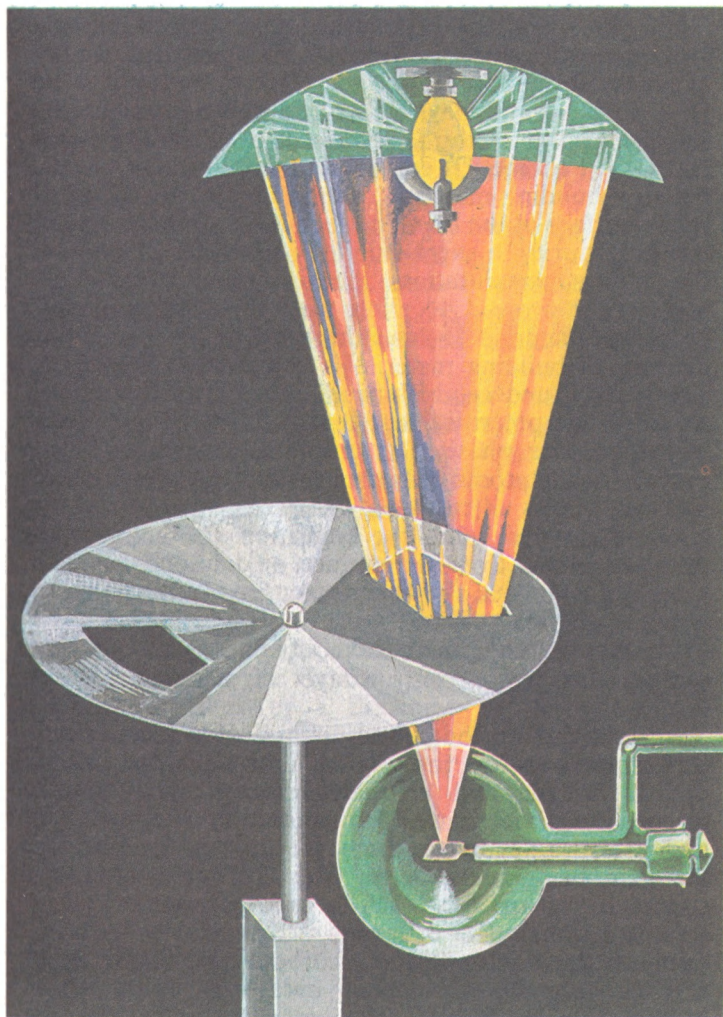
steps, which are abundant on the surface of a real crystal. Thus, the real structure of the surface is revealed in growing new diamond (at the initial stage). This revealing of the real surface structure of a crystal by forming microcrystals of other substance on it is called decoration.

More and more tiny diamond films form on the crystal surface; this is the second stage of growth. Then in the third stage they merge, forming a united front of crystallization. Special structural investigations showed that the buildup layer of diamond in no way differs from the substrate.

Pulse method of diamond buildup. As in the synthesis of other, already discussed, diamond crystals, the lower the growth rate, the better the quality (more perfect) the diamond film obtained. Conversely, the structure deteriorates when the rate of growth is increased. Usually, upon rapid supply of building material, graphite is deposited on the seed crystals. It must be removed in order to continue diamond growth. This is sometimes done by wet methods, boiling the crystals, for example, in perchloric acid. The acid boils and decomposes, giving off atomic oxygen at approximately 200°C. At this temperature atomic oxygen practically does not interact with diamond, but readily gasifies graphite. After removing the graphite, the crystals are washed in distilled water, dried, weighed and placed into the reactor.

Cleaning the seed crystals is quite obviously an additional operation of this process. Can it be eliminated?

Pulse method of diamond buildup. Shown above is the optical furnace. The sphere-shaped quartz reactor is shown below, and the chopper mounted on a base at the lower left.



The investigators then turned their efforts to the development of diamond growth techniques that simply avoid the formation of graphite. This turned out to be possible in several ways. Historically, the first was the so-called pulse method, proposed by B.V. Derjaguin and D.V. Fedoseev. It consists in the following. Assume that the building material, carbon atoms, are supplied to the surface of the diamond face in a surplus amount, but only during a short length of time. As a result of the high supersaturation, the formation of graphite nuclei may proceed together with the "autoepitaxial" growth of diamond. If this is followed by a pause or the delivery of building material is somewhat slack, then, owing to "undernourishment", the graphite nuclei revert to the precritical size and are transformed back to the gaseous phase. The graphite can, for instance, unite with the atoms of hydrogen that are present, and form molecules of methane.

On the other hand, the transition to the gaseous phase of atoms from the surface of diamond is much more difficult due to their stronger, "autoepitaxial" bonds with this surface.

Upon repeated alternation of pulses of supersaturation and pauses, only a layer of diamond is built up.

Experiments on the pulsed method of synthesis were performed with an installation that consisted of an optical furnace and a quartz reactor. The optical furnace is a device in which the radiation of a powerful, high-pressure xenon gas-discharge tube is focussed on the item being investigated. This furnace heated the specimens up to 3500°C. The quartz reactor was of spherical shape. The diamond seed crystal was at the centre of the reactor within a carbonaceous medium. It was clamped by means of needle-shaped rhenium holders. Up to 2000°C rhenium has practically no

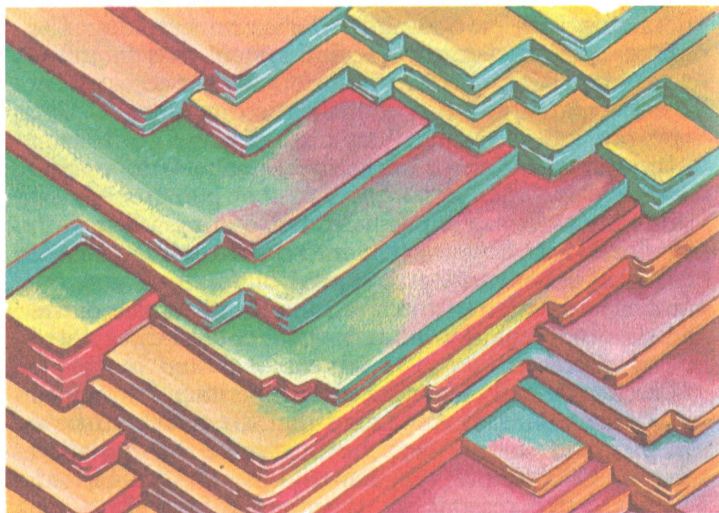
interaction with carbon and it forms no carbides. The reactor, connected to the vacuum system, was mounted on a supporting member that could be adjusted in three mutually perpendicular directions. The temperature was regulated by changing the position of the crystal with respect to the focal point of the optical furnace.

Heating pulses were produced by rotating a disk with slots (called a chopper) that interrupts the rays of the xenon tube. By varying the speed of rotation, and the number and length of the slots, the length of the pulses and that of the pauses between them could be regulated in a wide range.

These specially conducted experiments yielded interesting results. It was found that the temperature of the diamond surface in a heating pulse by radiation reaches 2500°C , but the diamond is not graphitized. There are two reasons for this: in the first place, the heating time is extremely short (about one hundredth of a second); and in the second place it was found that in a carbonaceous medium even a heated diamond crystal is not graphitized up to very high temperatures. In this way, the rate of reaction was considerably increased, and no graphite was deposited.

Diamond films of a thickness up to 12 or 15 micrometres were produced by the pulse method. In their properties they in no way differed from the diamond substrate and were its continuation. Unfortunately, growth of diamond is impeded by one of its own properties.

To heat a crystal or, to be more exact, its surface to a high temperature it is necessary for it to absorb radiation. But diamond crystals, on the contrary, pass visible light well, and this is the light mainly produced by the xenon tube. This made it necessary to treat the crystal surface before the experiment by giving it a mat,



Process of surface buildup on a crystal (under a microscope).

or dull, finish, and enabling it to absorb a part of the rays. As a result, the heating was more efficient.

But, as the crystal grew, the initial roughness decreased and, finally, the diamond became transparent again. It was no longer heated by radiation and its growth stopped.

Besides the pulse method for preventing graphite deposit in diamond growth, we can make use of the different capacities of gases to interact with different forms of carbon. We have already mentioned the fact, for example, that diamond is only poorly gasified by atomic hydrogen, whereas graphite is readily reverted back to the gaseous medium. If we devise a medium in which carbon is deposited and graphite is gasified, only diamond would grow.

American scientists proposed that such metals as platinum and palladium be used because they facilitate the formation of atomic hydrogen from its molecules. Other methods of obtaining atomic hydrogen also exist. But this one makes it unnecessary to provide a diamond substrate; diamond nuclei can also be formed on other substrates. Nevertheless, the process of diamond nucleation is less probable than the formation of graphite nuclei. However, if the latter are removed (gasified) only diamond will grow. The realization of this process enabled diamond films to be synthesized on metals and semiconductors, and individual diamond crystals to be grown, for instance, on a copper substrate.

At this point the reader may quite naturally ask the following question: can we do without any solid substrate at all, obtaining diamond directly from the gaseous phase, for example, from hydrocarbons, like we produce thousands of tons of carbon black? Strictly speaking, in the decomposition of, for instance, acetylene we should obtain graphite rather than carbon black, because graphite is a more stable form of carbon. Nevertheless, it is a matter of fact that acetylene carbon black is produced in large amounts and is used as a filler in rubber goods (mainly in automobile tires).

It follows from the theory dealing with the formation of nuclei of various crystal modifications having the same chemical composition that each modification corresponds to its region of supersaturation. In this region the probability of formation of the given modification becomes maximal. For diamond this is a region of very high supersaturation, which can be reached at high temperatures in a sufficiently dense gas. We can imagine the following (so far only hypothetical) experiment. The powerful radiation of a laser is instantly concentrated within a liquid. At this point



Growth of threadlike single crystals of diamond. They are called diamond “whiskers” and possess unique properties: perfect structure, the capacity to retain flexibility at high temperature, and high strength.

a laser break-down occurs, similar to an electric spark. The liquid hydrocarbon goes over to the gaseous state. A bubble is formed in which, at the initial instant, the temperature and pressure are sufficiently high for diamonds to be formed.

Threadlike whiskers of diamond. In investigations of the pulse method of diamond growth, co-workers of the

Physical Chemistry Institute, B. V. Derjaguin, D. V. Fedoseev, V. M. Lukyanovich, B. V. Spitsyn, V. A. Ryabov and A. V. Lavrentyev, discovered threadlike crystals of diamond. This event was duly entered into the USSR Register of Discoveries.

We already know that when the supply of building material to the growing face is sufficiently slow (because of a low supersaturation of carbon atoms near the face), the crystal maintains its monocrystalline structure in the process of its slow growth. Layers one atom thick are consecutively deposited, continuing the structure of the substrate. The "bricklaying" of each new layer is delayed until the preceding layer is finished. This delay occurs because a small island of the new layer is as unstable as a subcritical nucleus, and requires time to become established. The preceding layer, however, manages to become completely formed during this delay time.

If the building material is too rapidly supplied, the delay in the formation of a new layer is shortened. Such a layer begins to grow before the "bricklaying" of the preceding layer is finished. As a result, the facets of the crystal are no longer smooth and its structure ceases to duplicate the structure of the substrate. Eventually, the buildup layer becomes polycrystalline, i.e. it consists of many fine crystals.

But it sometimes happens that at certain spots on the surface of the crystalline facet growth continues without any delays and, at the same time, without spoiling the monocrystalline structure, even at extremely high rates of growth. As a result, threadlike crystals, or whiskers, of diamond, of very perfect structure, are grown at the corresponding places. Such single crystals have a length of one or two millimetres and were grown by the pulse method in about five hours.

Threadlike single crystals of diamond are sometimes referred to as materials of the future. They possess unique properties: perfect structure, the capacity to retain flexibility at high temperature, and, what is most important, high strength, close to the theoretical value. The theoretical strength of a material is determined by the nature and the strength of the bonds between its atoms. But in commonly employed materials, the actual, or engineering, strength is far short of the theoretical value, which is substantially reduced by the presence of various kinds of defects in their structure, such as incipient cracks. This can be illustrated by the following striking example. The tensile strength of ordinary iron is 18 to 23 kg/mm², i.e. it is sufficient to apply a force of 23 kg to 1 mm² to rupture this metal. But the tensile strength of threadlike monocrystals of iron (also called whiskers), 2 micrometres in diameter and 2 mm long reaches 1300 kg/mm².

Owing to their advantageous properties, threadlike crystals and filamentary materials are finding wider and wider applications in up-to-date engineering in the most critical units of machinery and apparatus. Threadlike crystals of sapphire, for instance, reinforcing niobium (in a proportion of 50 percent by weight), increase the strength of the component (compared to pure niobium) by a factor of four and, at the same time, reduce its weight. This is of prime importance for aerospace instrumentation engineering. In reinforcement, the filament provides a relatively rigid framework that carries the main load. Besides holding the filaments together the bond also protects them against the effect of the environment.

Threadlike single crystals are sometimes called whiskers because they can grow very thick, even more dense than genuine whiskers. Since many filamentary materials in composition adhere poorly to the binding

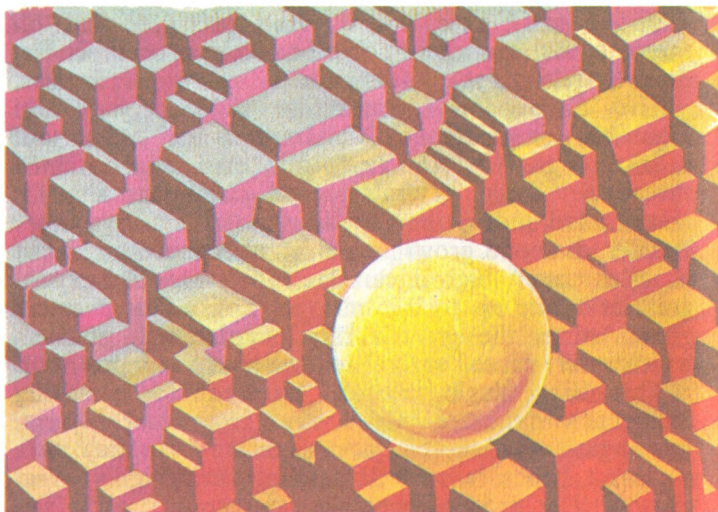
material, small threadlike crystals are deposited on them to increase their cohesion. This process is frequently referred to as "bristling" or whiskerization.

The discovery of threadlike single crystals of diamond, or diamond whiskers, is an important breakthrough. For the first time man has obtained threadlike single crystals of a substance that is metastable under the conditions of its synthesis. Besides, diamond growth occurred at low pressures, but at an extremely high linear rate. The threadlike crystal grew at a rate up to 0.25 mm per hour. This is much greater than the growth rate of diamond powders which rarely exceed several tens of angstroms per hour.

Threadlike single crystals of diamond are long filaments that are frequently twisted or bent. Investigations of these crystals indicate that they have a perfect structure, notwithstanding their highly rapid growth. The growing crystals can capture impurities and be coloured by them. An admixture of copper, for example, gives the diamond whisker a blue colour. The whiskers usually grew to lengths of 100 to 200 micrometres, but "record" lengths up to 2 millimetres were sometimes reached.

The first threadlike single crystals of diamond were produced by the pulse method. Subsequently, they were obtained by other methods as well. These included synthesis at high pressures and growth in an electron microscope.

Interesting observations were made by scientists in the Physical Chemistry Institute of the USSR Academy of Sciences. The growth of threadlike single crystals was arranged so that the surface of the crystal could be observed directly under a microscope during the experiment. In one of the experiments the investigators watched a growing threadlike crystal. Soon, however, it stopped growing in length and began



Isometric crystals of diamond. Sometimes, along with the threadlike crystals, spherical crystals are grown on the surface of the seed crystal.

growing in breadth. At the end of the experiment it was found that this tiny crystal of diamond is a single monocrystal of a diameter of about 0.1 mm with clearly defined faceting. Such monocrystalline formations were later often found in the pulsed crystallization of diamond. It is, of course, an alluring prospect to grow, not a whisker, but a whole crystal at a high rate and to reach a large size. But, so far, this is not possible; the growth mechanisms for threadlike single crystals and for diamond facets differ in many ways.

Graphite whiskers. Of all the known threadlike crystals, the most indestructible is the graphite whisker. It is strange, is it not, that graphite, so weakly bonded that we write with graphite (lead) pencils, has such high tensile strength? This is true, but in graphite whiskers the basal planes of the graphite, along which pieces so easily split off and leave a trace in writing with a pencil, are located along the whisker. If, for example, we take a sheaf of paper we can readily see that one sheet can be easily displaced by sliding it along the others. This, to a certain extent, is a model of the graphite used in pencils. But just roll several sheets as tightly as possible into a tube. Now we obtain a very rough model of a threadlike crystal of graphite. It is doubtful that you can now tear apart this paper tube.

Like this model, threadlike crystals of graphite have a high tensile strength. Crystals with a diameter of one micrometre have a tensile strength of about 1500 kg/mm².

Graphite whiskers have an astounding diversity of shapes. They can be straight, bamboolike with hollows inside, bent, and form a right- or left-hand helix. The great variety of shapes of the crystals is associated with the conditions under which they were obtained.

So-called graphite fibers, produced by the graphitization of polymer fibers at high temperatures, have only a slightly lower tensile strength than graphite whiskers. These fibers are used to make textiles that possess high tensile strength and can withstand high temperatures.

In addition to diamond, graphite and their modifications, other forms of carbon are also feasible. A team of Soviet scientists (A. M. Sladkov, V. V. Korzhak, Yu. P. Kudryavtsev and V. I. Kosatochkin) discovered a new form of carbon, which they named carbin. Diamond, as we know, has a three-dimensional



structure, graphite has a lamellar structure, whereas carbin has a chain structure. The properties of this modification of carbon are not yet fully known, and important discoveries are possible in this line.

The last three chapters have acquainted us with the synthesis of monocrystals of diamond. But polycrystalline diamonds are also found in nature. This poses the question: are scientists developing methods for the commercial production of synthetic polycrystalline diamond?

Polycrystalline Diamond Materials

Synthesized polycrystalline materials. Diamonds of the ballas and carbonado types, found among natural diamonds, are polycrystalline formations. They usually consist of small monocrystals of diamond joined together. For certain engineering applications polycrystalline materials are preferable because, in contrast to monocrystals, they are isotropic, i.e. their properties are the same in various directions. Of especial promise are polycrystalline ultrahard materials. They can replace diamond monocrystals in practically all cutting tools, even ones in which large natural single crystals of diamond are employed: drill bits for oil drilling tools, single-point lathe and planer tools, and wire-drawing dies.

Natural diamonds of the carbonado type are an aggregate of fine diamond particles. The size of the particles ranges from fractions of a micrometre to tens

Whiskerization of graphite fibers. The surface of each graphite fiber is coated by numerous small threadlike graphite crystals.

of micrometres. Natural carbonadoes are porous to some extent due to the intervals between the particles. Their density is therefore less than that of diamond monocrystals and ranges from 3.1 to 3.4 g/cm³.

At the present time, synthetic polycrystalline ultrahard materials can be produced by either of two methods: directly in synthesis or by sintering diamond powders.

The first method of producing synthetic carbonado requires the nucleation of a great many fine crystalline particles which should grow together before reaching any appreciable size. This problem was solved by a team of scientists of the High-Pressure Physics Institute of the USSR Academy of Sciences, headed by L. F. Vereshchagin, as follows. Graphite was subjected, in the presence of metal, to high pressure (at least 80 kilobars) at a temperature of about 1200°C. Since at high pressures the transformation of graphite into diamond proceeds with the evolution of heat—heat of crystallization—it was necessary to remove the evolved heat in order to speed up the process and, consequently, to increase the crystals being formed. For this purpose a metal bar is inserted into the graphite cylinder. The ends of the bar are in contact with the cooled parts of the pistons. To obtain a polycrystalline aggregate of a definite shape after synthesis, a graphite model of the required shape can be used as the blank. The model need only to be recalculated to take into consideration the shrinkage that occurs when graphite is transformed into diamond.

Besides synthetic carbonado, diamonds of the ballas type were also produced in the High-Pressure Physics Institute. These latter have a radial ray arrangement of the diamond grains, and are crystallized in the shape of a sphere.

In strength, synthetic ballas and carbonado are in no

way inferior to natural diamond. In their capacity for work, oil-well drilling bits, or crowns, set with crushed synthetic carbonado are even more efficient than those set with natural diamonds.

To be quite fair, however, it should be mentioned that for drilling operations under especially severe geological conditions, natural diamonds or materials based on them are being used as previously. This is not associated with any properties of synthetic carbonado, but, more likely, with the techniques applied in manufacturing the drilling bits. The body of the bit, i.e. the matrix into which the diamonds are set, is made of highly refractory metals and, consequently, prolonged heating at very high temperatures is required in manufacturing the bits. But synthetic carbonado includes a considerable amount of admixtures of metals used in synthesizing the diamonds. Upon heating, these admixtures interact with the diamond grains and the polycrystalline material loses its strength. Unfortunately, the strength is not restored when the bit is cooled.

The relatively low high-temperature strength of synthetic carbonado, i.e. its decreased strength upon being heated, compelled investigators to search for new techniques to obtain polycrystalline materials with high high-temperature strength. It was obvious that this method could be the sintering of fine diamond powders at high pressures. This possibility had been mentioned in the works of O.I. Leipunsky as far back as 1939.

Sintered diamond materials. These materials are usually called compacts or sinters, because compact specimens are obtained in sintering diamond powders at high temperatures. Practically all techniques for manufacturing compacts provide for the application of a metallic or carbide bond. The point is that the

deformation of diamond at even very high pressures and temperatures is practically negligible and, to obtain a strong and wear-resistant material, it is necessary to fill the voids between the diamond grains.

In heating a mixture of diamond powder with the powder of the binding material, the latter should melt and interact with the diamond, forming carbides. The compact that is finally obtained will possess high strength only when there is a transition layer between the diamond and the bond that is chemically active with respect to both diamond and the binding material. Hence, of prime importance for proper behaviour of the bond is its chemical interaction with diamond.

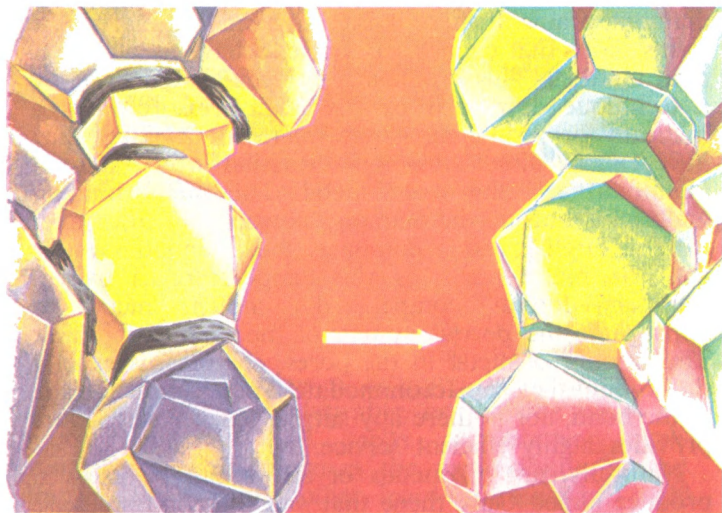
The investigator faces a dilemma in selecting the binding material. It is desirable, on the one hand, to take a material that melts at relatively low temperatures. This improves the producibility of the compact. But, on the other hand, sinters with such bonds cannot withstand the high loads they may be subject to, for instance in machining operations, because the bond is softened at the high cutting temperatures common to such operations. Moreover, readily fusible bonds, as a rule, have low hardness. This being so, might it not be to advantage, one would think, to use refractory borides, carbides or nitrides as the binding material? But such materials, having high hardness, are themselves not readily deformed. Hence, they cannot efficiently fill the voids in the sintering process. Besides, compacts made of diamond with a refractory carbide, nitride or boride bond are very brittle. Such sinters are extremely rarely used in regular industrial practice. In any case, there are no reliable data available on their application.

It is very important to properly determine the amount of binding material required for sintering. It is obvious, of course, that with insufficient binding

material some unfilled pores remain between the diamond grains. If there is excessive binding material it forms blobs that cannot, of course, behave as an ultra-hard material. This problem was ingeniously solved by a technique developed by the High-Pressure Physics Institute for producing a new material: a sinter they have called "almet", from the Russian word "almaz" (diamond) and the word metal. The metal binding material is outside the diamond powder, but in contact with it. High pressure compacts the diamond powder and the metal melts as the temperature is raised. Capillary forces "compel" the molten metal to impregnate the porous system of the diamond grains. The amount of metal in the pores, or voids, is exactly the amount they can accommodate. There is no shortage in the bond, nor is there any surplus; as a result, almet provides highly efficient service.

Naturally, not all metals or alloys can be used to produce almet. Only those that wet diamond well are suitable. Of interest is the fact that if diamond powder is mixed with a powder of copper, which does not wet diamond at all, all the copper runs out of the diamond powder in sintering, forming a layer at the boundary of the diamond sinter.

Naturally, the best bond for joining diamond grains into a single compact item would be diamond itself. But extremely high pressure and temperature are required to deform diamond so that it fills all the pores. Such pressures and temperatures are feasible with up-to-date engineering techniques. But, unfortunately, the refractory dies (devices for producing the required pressure) become inoperative so quickly that the whole idea is not worth-while. As a matter of fact, the purpose of the sintered polycrystalline diamonds is to replace cemented carbide in a cutting tool and, if too much cemented carbide is required in sintering the diamond, the process becomes inexpedient.



Transformation into diamond of thin layers of graphite located between diamond crystals.

The required parameters of the sintering process can be reduced to some extent by resorting to various contrivances: the introduction of special admixtures (not binding materials!), preliminary treatment of the diamond powders, etc. According to a manufacturing process developed by the USSR Institute for Refractory Metals and Cemented Carbides, the powders of natural and synthetic diamond are first calcined at a temperature from 500 to 600°C. Then, in the presence of a compound (lime, fluorite, chalk or talc) of alkali-earth metals, the powders are sintered at a pressure of 120 to 170 thousand atmospheres and a temperature from 2700 to 3700°C for a time not exceeding 2 seconds. The

sinters obtained in this process are designated by the letters CB. They are employed in manufacturing single-point cutting tools. Crushed polycrystalline compacts CB are also used in oil-drilling bits.

Unfortunately, these compacts are sintered at very high pressures and at temperatures complying with the curve of phase equilibrium, which also increase the cemented carbide consumption. Hence the possibility of producing large compacts is extremely limited.

A new method of obtaining diamond compacts at pressures not exceeding 80 thousand atmospheres was developed by the Physical Chemistry Institute of the USSR Academy of Sciences and the Institute for Ultrahard Materials of the Ukrainian Academy of Sciences. The main principle of this method is based on the phase transitions in thin layers of graphite applied to the surface of diamond. It is known that the surface of a crystal substrate substantially affects the properties of thin layers applied to it. According to the calculations of specialists, a thin graphite layer, squeezed between two diamond crystals, is transformed into diamond at much lower pressures than indicated by the Leipunsky curve. The effect of pressure reduction in the phase transition decreases as the thickness of the graphite layer is increased and, in the limit, at a considerable thickness, equals zero. In other words, thick graphite layers fully comply with the well-known Leipunsky relation.

Besides the reduction in the pressure required for the graphite-diamond transition, the process of collective structural rearrangement is facilitated in thin layers. This enables graphite to be transformed into diamond in a short time, equal to several seconds. This process of producing diamond compacts consists of two stages. In the first the diamond powder is grown from the gaseous phase. This should include the growth, not

only of diamond and diamond-graphite layers, but that of a pure graphite layer as well. The second stage consists in the sintering of the grown powder in the region of diamond stability. The sintering pressure is relatively moderate, enabling compacts up to several carats to be produced. This new material has been named carbonite (from the word "carbon") because it consists of nothing else but carbon. Carbonite has a high high-temperature strength, i.e. it does not lose its strength after being heated to high temperature, because it has no foreign inclusions.

Tests in which carbonite was used as the cutting material for single-point tools that machined non-ferrous metals and cemented carbides demonstrated that this new material is capable of providing long tool life in conjunction with an excellent surface finish. Carbonite also shows promise for application in oil-drilling bits, truing and dressing tools for abrasives, and in drawing dies.

None of the synthetic polycrystalline materials, of course, has such a regular structure as a monocrystal of diamond. The grain boundaries of the initial diamond powder have properties that are entirely different from those of the particles themselves. Visible under high magnification on the sharpened cutting edge of diamond compacts are the saw-shaped teeth of the initial grains. There are no such saw-teeth on the sharpened cutting edge of a monocrystal of diamond.

Boron nitride. Our account of polycrystalline ultra-hard materials will be incomplete if we do not mention boron nitride. This chemical compound is not found in nature; it was synthesized by analogy with the forms of carbon: graphite corresponds to the graphite-like boron nitride and diamond with a cubic

lattice, to cubic boron nitride. Lonsdaleite also corresponds to a modification of boron nitride. The difference between the densities and the shortest distance between the atoms in diamond and in cubic boron nitride is less than 1.5 percent. Cubic boron nitride, like diamond, is an ultrahard material. It is obtained from graphitelike boron nitride by synthesis at high pressures and in the presence of catalysts.

The ultrahard modifications of boron nitride are employed as abrasives but, most frequently, in polycrystalline compacts. Single-point cutting tools for machining, tipped with boron nitride, have many advantages compared to diamond tools. Boron nitride does not enter into chemical interaction with iron, and can thereby be used to machine steel and ferrous metals, including even the hardest heat-treated steels, which is a very valuable feature in engineering.

It is regular practice in manufacturing processes in the engineering industries to first machine a blank for some workpiece and then subject it to heat-treatment to impart high hardness (and, thereby, wear resistance) to its surfaces. For example, the thread is first cut on drill pipe for deep-hole drilling and then the pipe is hardened by some kind of heat-treatment. As a result of this hardening process, owing to inevitable nonuniform temperatures of the pipe, certain dimensions of the threads are distorted. After checking the threads, some of the pipes must be rejected. This can be avoided by employing single-point thread-cutting tools tipped with boron nitride; they can be used to cut the thread after hardening.

Another vital advantage of tools tipped with boron nitride is their resistance to impacts. They are therefore used in impact cutting, for instance in machining a surface interrupted by grooves or holes. This property

of boron nitride guarantees its widespread application in the machining of metals.

Thus, as we have seen, new ultrahard materials have been synthesized. Synthetic diamond and boron nitride have been placed at the service of mankind. Just how important is the position they occupy in up-to-date science and engineering?

Science, Engineering and Synthetic Diamond

Contribution of synthetic diamond to science and engineering. Year by year these concepts become more and more closely interlinked. The contribution of science and engineering to the history of diamond steadily increases; more and more new applications of this marvelous crystal are found in various fields. You have already read in our book of the trades and professions of this "King of the Minerals" and have become acquainted with the sequel to its history, written by the men who have synthesized this crystal. It remains, now, to relate the new opportunities offered by synthetic diamond to science and engineering.

With the invention of methods for the growing of diamond and their application in regular production, the volume of diamond used in engineering has substantially increased. In this connection, synthetic diamond is more and more persistently crowding out the use of natural industrials. Thus, in the USSR in 1962, the amount by weight of natural industrial diamonds that were made use of was equal to the amount by weight of synthetic ones, whereas by 1971 the share of synthetic diamonds had already increased to 85 percent. And this share continues to grow because up-to-date large engineering plants employ hundreds of

thousands of carats of diamond annually in the manufacture of hundreds of items. The increase in the percentage of synthetic diamonds is facilitated to a considerable extent by their lower cost. In the world (without including the USSR), for instance, synthetic diamonds amount by weight to 80 percent of all diamonds, whereas their cost amounts to 25 to 30 percent of the total cost of all diamonds.

In recent years, the requirements made to various manufacturing processes and operations have become considerably more strict. This concerns, among other matters, the quality of the machined surface of various materials. As is known, the lower the height of the microirregularities (ridges) on a machined surface, the higher the grade of surface finish. Surface quality standards adopted in various countries indicate either the arithmetic average deviation of the surface microprofile, the height of irregularities or the maximum height of irregularities. The lowest arithmetic average deviation of the surface profile from a mean line for diamond machining (turning and boring) is equal to 0.1 micrometre. Methods used today for machining metals, for instance, provide for techniques enabling the highest required finish to be obtained in the first machining operations. It is therefore desirable to obtain a surface in the cutting (chip removal) operations that does not require subsequent grinding and polishing. This can be done by means of a cutting tool tipped with synthetic diamond.

Before we begin to manufacture a diamond tool, however, it is necessary to determine exactly what kind of a diamond is required. Synthetic diamonds, like natural ones, are used chiefly in the form of powders. Each powder has its characteristics which are specified (in the USSR) by the corresponding State Standard. According to the pertinent USSR standard, diamond

powders are divided into two groups: abrasive powders and micropowders. Roughly speaking, the first group includes diamond powders with a particle size over 60 micrometres and the second, with a particle size under 60 micrometres.

The grain size of a diamond powder plays a vital role in its application in practice. If a diamond powder is to be used to obtain smooth surfaces it should be very fine. Coarser grain sizes are suitable for rough abrasive machining.

At the present time, several grades of diamond abrasive powders are being manufactured from synthetic diamond in the USSR.

Grade ACO diamonds are synthesized under conditions that ensure a predetermined brittleness, strength and developed surface of the particles. These powders are used for tools having an organic (resinoid or rubber) bond and designed for finishing and lapping operations. The high brittleness of the ACO powders leads to the formation of new and sharp cutting edges even upon only slight dulling of the grains. This feature provides for a kind of self-dressing (sharpening) of the abrasive tool. Self-dressing abrasive tools operate with a low cutting force and, consequently, at a low grinding temperature.

Grade ACP diamonds are about twice as strong as those of grade ACO and are less brittle. They are used for making tools with vitrified or metal bonds.

Grade ACB diamonds have still higher strength and are used for tools operating under high loads.

In brittleness and strength ACK diamonds are identical to natural diamond and are well faceted. They are manufactured of a size up to 500 micrometres. Tools with such diamonds are used under especially severe conditions, for example, in cutting and working natural rock and reinforced concrete.

The typical features of ACC diamonds are minimum brittleness and maximum strength, exceeding even the strength of natural diamond. They are manufactured in sizes up to 630 micrometres. Along with industrial natural diamonds they are used in oil-drilling bits, for truing and dressing grinding wheels and for cutting corundum and even diamond itself. As a rule, ACC diamonds are transparent, well-faceted monocrystals.

Grade ACM and ACH diamond powders are used to prepare suspensions and pastes. They can be used for lapping and other fine abrasive machining operations. Very thin cut-off wheels are made with micropowders by electroplating techniques. These wheels find efficient application in microelectronics. Diamond micropowders can produce the highest class of surface finish; this is a vital feature in making the components used in microelectronics, optics, and in finishing the mirrors for lasers.

Diamond powders are sorted into narrow fractions based on the grain size. Abrasive powders are sorted by means of sieves, and micropowders (also called sub-sieve powders) by means of a centrifuge. For example, the grade designation ACC 630/500 indicates that we are dealing with grade ACC diamonds in which the predominant grain size ranges from 500 to 630 micrometres; grade ACM 2/1 is a diamond micropowder with the predominant grain size ranging from 1 to 2 micrometres, etc. In connection with problems posed by the most up-to-date engineering techniques, development work is being done for the regular manufacture of powders with even finer grain sizes, so-called submicropowders. Powders with grain sizes of 0.7, 0.5, 0.3 and even 0.1 micrometre have been obtained.

This means that the chief size of the particles in such a submicropowder should not exceed 1000 angstroms.

The requirements made to micropowders, and especially to submicropowders, are incomparably higher than those made to the coarser abrasive powders. It is obvious that even a single coarse diamond grain in a submicropowder can reduce all of its superior quality to zero. As we know, fine powders are designed for the last finishing operation by super-finishing, lapping, honing, etc. The surface roughness after such operations is measured in fractions of a micrometre. All of a sudden, on the finished surface the inspector sees bright deep scratches made by the single coarse grain that in some unknown way got into the micropowder. This leads to the loss of the labour of a large number of men over many days.

One should not think that the larger the grain size of a diamond powder, the more expensive it is. This is not so at all or, to be more exact, it is so down to a definite grain size. But the finest micropowders cost more than the coarser ones, and the submicropowders have the same price that the largest synthetic diamonds do (not per grain, of course, but per carat).

These price anomalies are caused by the difficulties encountered in eliminating particles exceeding a definite size in a centrifuge.

In addition to mechanical engineering (machine tool, aviation and shipbuilding industries), a large-scale consumer of diamonds is geology, in which the output per carat of diamond used in drilling is especially high. The excellent features of polycrystalline diamond materials are well known in geology and other branches of the national economy. It was found that diamond compacts (in drilling bits, truing and dressing tools for abrasive wheels, etc.) can be most efficiently manufactured by sintering coarse powders of a grain size from 10 micrometres and larger. It proves good practice to use a thoroughly mixed combination of

coarse and fine fractions of the powder; the fine particles then fill the voids between the coarse ones.

Diamond powders have found their most extensive use in wheels for grinding metals. An especially efficient technique in this field is the introduction of surface-active metals into the powders. This idea was proposed by E.D. Shchukin and V.N. Pertsov to speed up the grinding process and to extend the service life of the grinding wheels. This technique is based on an effect discovered by P.A. Rebinder, member of the USSR Academy of Sciences, and consisting in the facilitation of the disintegration of solids (in our case, the removal of metal from the surface being ground) by the adsorption of surface-active molecules.

It is quite obvious that the application of diamond tools requires the use of suitable up-to-date machine tools. It is absurd to mount a diamond-tipped tool in an obsolete, worn-out lathe that may, in addition, be out of order. The application of diamond tools requires advanced production facilities at a generally high level of development. On the other hand, high-precision and high-output machine tools require cutting tools with ultrahard materials specifically to enable them to maintain high machining accuracy and a high production capacity. If the cutting tools were not up to these high standards, and could not provide for a sufficiently long tool life, it would be necessary to stop the machine tool or a whole automatic transfer line every five minutes to change dulled tools.

It is necessary, here, to mention still another important application of diamond. Nearer the beginning of this book we wrote about the anvils of Percy Williams Bridgman, a pioneer in high-pressure physics. These anvils enabled him to attain such high pressures for the first time. The synthetic diamond, itself, is, to a great extent, the creation of high

pressures. And diamond, it turned out, can also do much for the further development of high-pressure techniques. Such an interrelation, or feedback, is typical of the rapidly developing science of our time and of the revolution in science and engineering.

In 1959 it was proposed to replace the anvils of cemented carbide by diamond anvils. The first such instrument consisted practically of two brilliant-cut diamond bodies with their apexes sliced off. Along the plane surfaces thus obtained, the diamonds were pressed together by a system of levers and springs. Calculations indicated that pressures exceeding a million atmospheres could be produced between the planes of contact of the diamonds when they are pressed together.

Devices with diamond anvils were quite simple and are being improved up to the present time. The problem, however, of determining the true pressure between the anvils, i.e. calibration of the device, was posed from the very beginning. This problem was solved in 1972 when variations in the absorption spectrum of ruby were used to measure the pressure. As the pressure is increased, one of the lines in the ruby spectrum is shifted in accordance with a definite relationship. This shift can be readily measured by modern instruments—spectrographs—to determine the pressure. Hence, along with the materials to be investigated, a small piece of ruby is placed between the diamond anvils. What a truly interesting combination of diamond and ruby, especially when we take into consideration the fact that gold and platinum are frequently used for electric contacts in transitions to the metallic state.

Naturally, the attainment of high pressures is not an end in itself. In the first place it makes it feasible to investigate the states of various substances at high

pressures. This is a problem that has long attracted the attention of scientists engaged in a study of our earth. Not without reason do we complain, sometimes, that we know much more about the stars than about the structure of the planet we live on. According to up-to-date concepts the earth consists of the crust, mantle and core. The pressure at the crust-mantle interface (at an average depth of 100 km) is about 10 thousand atmospheres, that at the mantle-core interface (at a depth of 3000 km) is about 1.5 million atmospheres, and at the centre of the earth the pressure reaches 35 million atmospheres. The application of diamond anvils provides scientists with a powerful means, primarily, of investigating the properties of substances in the earth's mantle.

Superhigh-pressure techniques can also be used to solve more common problems. These include the investigation of variations in the rate of radioactive decay as the pressure is increased, and of the properties of liquids and lubricants. In modern machinery the lubricant is subject to very high pressures, which may lead to seizure phenomena, in which case the lubricant no longer lubricates, i. e. it does not facilitate the sliding of friction surfaces. It was formerly thought that seizure phenomena are associated with the formation of large glasslike particles in the fluid lubricant. Investigations by means of diamond anvils led to the conclusion that a highly viscous film can be formed near the friction surfaces in thin layers of liquids. This film is what impedes the motion of friction machine components with respect to one another.

The fundamental application, however, of superhigh pressures reached by means of diamond, is in superconductivity research. At a definite temperature for each conductor, its resistance to electric current drops to zero. This phenomenon was discovered by

Heike Kamerlingh Onnes, the famous Dutch physicist, in 1911. In a superconducting ring, or loop, a direct current continues for a long time, because the electric resistance of a superconductor is less, at least by a factor of 10^{17} , than the resistance of the same conductor at room temperature. To understand how small a fraction of the resistance remains in a state of superconductivity it is necessary to divide one by a number in which the one is followed by seventeen zeros. What we obtain is practically zero.

Note, however, that superconductivity is reached, unfortunately, at extremely low temperatures, not exceeding twenty some degrees above absolute zero. This means that the conductors must be cooled by liquid helium. The development of superconductors capable of operation at high temperatures is still an unfulfilled aim of science. It is difficult to even imagine the vast significance of a superconductor that operates at high temperatures. This would mean energy transmission without loss over huge distances (today a substantial fraction of the energy in electric power lines is expended in overcoming the resistance), highly powerful electromagnets, etc. For these reasons, superconductivity research is being conducted widely all over the world.

Matter subjected to high pressures is transferred to the metallic state. The hypothesis was advanced in 1968 that metallic hydrogen may be a superconductor almost at room temperature. This started an avalanche of scientific papers devoted to the production of metallic hydrogen. In the Soviet Union this research is being carried out in the High-Pressure Physics Institute of the USSR Academy of Sciences. In 1972 scientists of this institute reported that they had obtained a transition of hydrogen to the metallic state at a pressure of one million atmospheres, using anvils of synthetic diamond.

The next problem in this field is to clear up the possibility of keeping hydrogen in the metallic state after removing the pressure, i.e. under ordinary conditions.

Also of interest is the transition of xenon, an inert gas, to the metallic state. The first chemical compound of xenon (with fluorine) was only obtained as late as 1961. Not long ago, a team of scientists of the High-Pressure Physics Institute, headed by E.N. Yakovlev, not only transferred xenon to the metallic state but, at a temperature only 7° above absolute zero, obtained it in the superconducting state. This required a pressure of 500 thousand atmospheres, which was produced in a special chamber made of polycrystalline diamond.

Contribution of science and engineering to diamond.

Advanced science and engineering are doing much to enable diamond to brilliantly demonstrate its unique properties. Note how all-powerful Science and Engineering aid the diamond, form and "dress" it along the whole length of its pathway, from nucleation to its workplace!

To a considerable extent diamond is called upon to replace cemented carbide cutting materials based on tungsten carbide, including Pobedit, one of the very first grades of such cutting materials developed many years ago in the USSR. But synthetic diamond is born between cemented carbide dies that are used in its synthesis.

To produce the pressure required in the process of diamond synthesis it is necessary to have the most powerful of presses, which are the embodiment of the most advanced ideas of science and engineering, a realization of the high skill and knowledge of workmen and engineers in industry. Exactly such is the press in operation in the High-Pressure Physics

Institute. This press is unique in size and capacity. It can develop a pressing force of 50 thousand metric tons, is installed in a separate building and a whole special freight train was required for its delivery to the Institute.

After its synthesis diamond is in a mixture with metal and the graphite that did not take part in the reaction. The metal and graphite are usually removed by various acid mixtures, subjecting the products of synthesis to their repeated action. The resulting diamond powder is then classified.

A great many types of cutting and abrasive tools are made of the various grades of synthetic diamond. Different types of bonds are used to hold the diamond grains in these tools.

Of prime importance is the mounting of diamonds in drilling bits, which are studded by the most expensive and largest crystals. Obviously, in the mineral prospecting, oil-well drilling and allied operations for which these bits are used, it is especially necessary for the tool to operate efficiently as long as possible. For better cohesion with the metal of the bit, the diamonds are first coated with a thin layer of metal. Before applying the metal, the diamonds are ovalized: all the faces of the crystals are rounded over, imparting an oval shape to the crystals. This operation, of course, leads to the loss and crushing of many diamonds, but ovalized diamonds give better service than the initial ones, because they have no projections. Such projections sometimes pull a diamond out of its seat in the tool.

Diamonds are investigated by the most up-to-date techniques used in research today: X-ray structural analysis, electron paramagnetic resonance (EPR), infrared spectroscopy, scanning and transmission electron microscopy, etc.

This account of how, at first, the chemical nature of diamond was cleared up, and then its structure; of how synthetic diamond was first produced at high pressures and then a method was developed for building up and growing diamonds from a gaseous medium, is a highly instructive history. It demonstrates the omnipotence of science (chemistry and physics, in particular), enabling mankind to develop processes and materials that one could not even dream of in the nineteenth century. This became feasible, however, not all of a sudden, but only after a sound scientific foundation had been erected.

The fundamentals of chemistry became the foundation that enabled the composition of diamond to be cleared up. Diamond structure became known after research methods were devised that made use of X-ray diffraction in crystals. The method of synthesis at high pressures is based on the progress made in the theory of phase equilibrium and transitions. Methods of synthesis in the region of diamond metastability were founded on the study of the mechanism for the formation of a new phase. Techniques and instruments for evaluating the grain size of powder are based on the application of the kinetic theory of gases and their filtration through porous bodies.

All the above-enumerated fundamental scientific developments were applied in practice for solving many problems having nothing whatsoever to do with diamond. But they will undoubtedly find further use for improving methods of diamond synthesis and investigation. There is also no doubt that for a further establishment of our knowledge of diamond, other fields of science will be required, both in fields already developed and those still awaiting development.

These statements clearly and convincingly demonstrate the supreme value of so-called fundamental scientific research, which enables extensive fields of

natural phenomena to be comprehended and put into the service of mankind. The practical results achieved in this process frequently, in their turn, are of benefit to the development of science itself.

The history of diamond is once again witness to the inexhaustibility of nature and the eternity of the pursuit of knowledge. We know very much about the diamond and have even been producing diamonds for many years but, at the same time, have still insufficiently investigated this mineral. For example, the properties of diamond-base polycrystalline ultrahard materials are still full of puzzles; their structure and the sintering mechanism are not completely clear. It is quite probable that structures are formed at the grain boundaries upon the application of high pressures that drastically differ from those known today. Scientists, for this reason, are giving much consideration and making every effort to reveal all the phenomena that occur in the sintering of diamond and boron nitride.

The relationship between different scientific schools and trends can be most clearly disclosed by using as an example the investigations on diamond synthesis, either by means of high pressures or gaseous-phase crystallization. Investigations in the mechanism of diamond formation in nature stimulate the conduction of new experiments in laboratories. On the contrary, the results obtained in laboratories facilitate the advancing of new ideas on the origin of natural diamond. In ending their book "The Origin of Diamond", the Soviet scientists V.G. Vasilyev, V.V. Kovalsky and N.V. Chersky wrote: "Discovery of the mechanism of diamond formation in nature is not only of theoretical interest; it also is of great practical value. The solution of this age-old problem will enable the best initial material to be found and conditions to be determined for the production of synthetic diamond

with prespecified parameters. It will also introduce clarity into the criteria for prospecting for diamond-bearing kimberlite pipes and deposits."

It is a well-known fact that new ideas often crop up on the boundary between different fields of science. Combining research in the fields of physics, geology and chemistry, the Soviet geochemist E.M. Galimov advanced a new idea on the formation of diamond, backing it with calculations of chemical reactions, the flow of molten magma, as well as calculations from thermal physics.

According to the theory advanced by Vasilyev, Kovalsky, and Chersky, the required pressure in the magma is produced by the explosion of a gaseous mixture, i.e. as the result of a very rapid chemical reaction. Galimov's theory contends that the pressure is produced by a purely physical cause, the formation of bubbles of carbonaceous gas, known as cavitation. Here extremely high pulsed pressures are developed in what could be called microexplosions. Cavitation is a phenomenon that is well known to scientists. It is what erodes the blades of rapidly rotating screws of ships. The surface of the blades becomes pitted with tiny craters. This phenomenon may occur upon sudden widening of a channel along which a liquid is flowing at high velocity, if the liquid contains dissolved gas. Galimov confirmed by his calculations that gas bubbles are formed in the molten magma and that their cavitation leads subsequently to a localized increase in pressure to millions of atmospheres and in temperature, to ten thousand degrees. Here the carbonaceous gas is decomposed and forms diamond. Such processes are repeated time after time. As a matter of fact, natural diamond displays a complex structure, as if one layer is grown on a previous one with several interruptions.

Both of these explosive theories enable certain

phenomena observed in nature to be explained: the productive capacity of certain kimberlite pipes and the complete absence of diamonds in nearby pipes; the formation of perfect crystals; the distribution of diamond in the rock; etc. The proposed mechanisms are also confirmed by experimental research conducted in the Physical Chemistry Institute.

The authors of the present book reasoned as follows. When hydrocarbons decompose, carbon black is formed rather than graphite, though carbon black is metastable with respect to graphite. This signifies that metastability in itself does not forbid the formation of carbon particles of various structural modifications. Calculations confirmed this supposition and, moreover, indicated that each structural form of carbon—carbon black, graphite and diamond—corresponds to a region of conditions under which its formation becomes predominant. We conducted an experiment in which carbon was crystallized in a bubble of vapour of liquid heated to high temperatures. The products of disintegration included fine crystals of diamond along with particles of graphite, carbon black and carbins.

Our book deals mainly with diamond and, only to a small extent, with other forms of carbon. These, however, are of prime importance as objects of research. But the authors would like to conclude their book with the statement that chemists can produce other items besides diamond. Examples are the production of other substances by crystallization from the gaseous phase in chemical reactions. We suggest that the reader regard our last chapter as a prologue to a new, as yet unwritten, book.

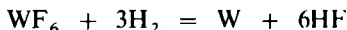
Not Only Diamonds Are Man-Made

Being a precious stone, diamond, in a certain sense, is a very special material. But the might and potentiality of chemistry is displayed no less brilliantly in the production of other ultrahard materials. An example is boron nitride, which is not found in nature, but has found wide application in recent years. An important role in modern industry is being played by pyromaterials, which are obtained by chemical crystallization from the gaseous phase at high temperatures (their name is from the Greek word "pyros" meaning a fire). Today a great many pyromaterials are produced in laboratories and chemical plants.

As a matter of fact, the first pyromaterial known to mankind is carbon black, or soot. Alexander Nikolayevich Lodygin, famous Russian electrical engineer and inventor of the incandescent lamp, obtained tungsten for the filament by disintegrating volatile tungsten chloride. One of the breakthroughs of the twenties was the iodide process for obtaining pure metals. It became the basis for the industrial production of plastic zirconium, titanium, hafnium, and other metals.

The fluoride process for obtaining tungsten was investigated in great detail and put into regular production in industry by A.I. Krasovsky and R.K. Chuzhko of the Physical Chemistry Institute.

This process is based on the reaction

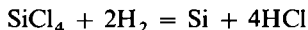


which, of course, does not represent a complete picture of the process. It follows from the research of the above-mentioned chemists that the depositing of

tungsten on the surface passes through a stage of activated adsorption of hydrogen. This, specifically, is the circumstance that makes it possible to run the process at 500 to 600°C. Note that the melting point of tungsten exceeds 3000°C and that the boiling point is about 6000°C. Nevertheless, so-called fluoride tungsten is superior in quality to tungsten obtained by powder metallurgy (by sintering tungsten powder under load at high temperature for a long time).

Gaseous-phase chemical crystallization is also employed to obtain such hard materials as titanium carbide in the disintegration of a mixture of titanium chloride, methane and hydrogen at 1200°C; or as aluminium nitride as an effect of a temperature of 1100°C on a mixture of aluminium chloride and ammonia in a stream of argon. In general, a typical feature in producing refractory materials by chemical techniques is that the temperature of the process does not exceed one half of the melting temperature. Chromium, for example, having a melting point of 1800°C can be obtained by disintegrating organic compounds of chromium at temperatures of about 300°C.

Considerable advances have been made in the deposition from the gaseous phase of such industrially important semiconductors as silicon. At a temperature of 1150°C silicon is obtained by the reaction



But if we add methane to the initial mixture, we can obtain silicon carbide at only 1000°C.

The application of pyromaterials has done much to develop new and more efficient techniques and to improve traditional ones, as well as instruments and tools. Thus, the application of thin layers of titanium carbide (of a thickness up to 10 micrometres) on the

surface of cemented carbide tips for single-point cutting tools increases their service life several times.

This short review of chemical methods of crystallizing various substances from the gaseous phase shows the high potentiality of such methods. It could be said that we are witnesses of the foundation of a new branch of industry. Since engineering requirements to the quality of materials becomes higher and higher, and they must be produced at the lowest possible cost, very much is yet to be done in this new branch of industry by scientists in this line.

TO THE READER

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*The Price of Truth: the Story of
Rare-earth Elements*

D. TRIFONOV, D. Sc. (Chem.)

This popular book written specially for teenagers by a well known historian of chemistry tells us about an astonishing family of chemical elements known as the rare-earth elements.

For many years scientists from various countries added bit by bit to our knowledge of the rare-earth elements. What is the number of the rare-earth elements? How to explain their fantastic similarity? How to fit them into the periodic system of elements? Many physicists and chemists tried to answer these questions. It was only some fifty years ago that the age-old mystery of the rare-earth elements was finally resolved.

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The reader will learn why solutions boil or freeze, why some substances dissociate into ions when dissolved in liquids, and how an electric current flows through a solution. The major part of the book is devoted to the physical and chemical properties of solutions.



Boris Vladimirovich Derjaguin, D.Sc. (Chem.), is an eminent Soviet scientist in the field of physical chemistry, and an associate member of the USSR Academy of Sciences since 1946. Dr. Derjaguin was born in Moscow in 1902 and graduated from the Physics and Mathematics Department of Moscow University in 1922. In 1935 he organized the Thin Films Laboratory in the Physical Chemistry Institute of the USSR Academy of Sciences. Dr. Derjaguin has written more than 900 papers in this area of physical chemistry. In 1958 he received the Lomonosov Medal from the USSR Academy of Sciences. Dr. Derjaguin was awarded an honorary degree by Clarkson College of Technology (NY). He is a member of the Carolinische Deutsche Naturforscher.



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